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METALLOGENY OF HEAVY OILS, NATURAL BITUMENS, AND OIL SHALES

By

Iosif S. Goldberg

Editors

Richard F. Meyer and Michael D. Belonin

Translator

Dorothy B. Vitaliano

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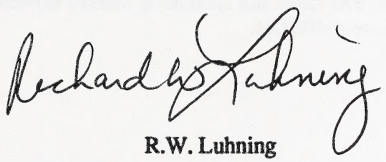
PUBLISHER'S NOTE

The Alberta Oil Sands Technology and Research Authority (AOSTRA) is pleased to publish this book, in collaboration with the U.S. Geological Survey. This joint effort was undertaken in order to bring to the outside world results of investigations done in the former Soviet Union on the extraction and use of rare metal by-products from the refining of bitumen, heavy and extra-heavy oil, and oil shale. Considering that the heavy oils of the world are becoming more attractive as the light oil reserves decrease, the increased production and upgrading of these heavy oils offer an attractive sideline in the removal and use of the heavy metals. Of further consideration is the positive environmental impact of removing the contaminating metals. The origin, distribution, and classification of deposits in the former Soviet Union are also covered. We trust that you will find the material contained in this book of interest and of value.



R.W. Luhning
Vice-Chairman and Executive Director
Alberta Oil Sands Technology and Research Authority
January 1994

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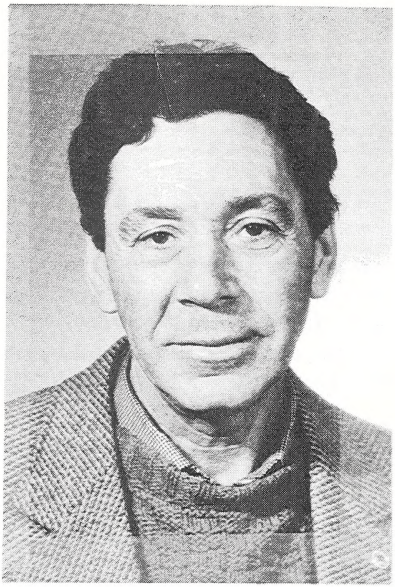

The author, Dr. Iosif Goldberg, has been a practicing petroleum geologist and geochemist for more than 30 years. From 1982 until 1983 he served as Head of the Laboratory for the All-Russia Petroleum Scientific Research Geological Exploration Institute (VNIGRI) in St. Petersburg.

He has carried out exploration research in Eastern and Western Siberia, Western Kazakhstan, and in the Timano-Pechora, Volga-Urals, and Pre-Baltic regions. His special field of research is heavy crude oil, natural bitumen, and oil shale, and the metallogeny of these fuels. He has evaluated the natural bitumen resources of the former Soviet Union, compiled maps of the metal content of the combustible mineral deposits, and predicted the nickel and vanadium content of heavy oil and natural bitumen worldwide.

Dr. Goldberg received his M.S. in petroleum geology in 1955 from the Mining Institute, St. Petersburg, and Ph.D. in 1968 from VNIGRI. He was presented an honorary Sc.D. in Geology in 1983. His work has been published in 75 reports as well as eight books and has been presented to eight international conferences.

Dr. Goldberg has resided in California since 1993.

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INTRODUCTION

New technologies have been developed that use the unique properties of many rare and disseminated elements, such as V, Re, Bi, Cd, Se, Tl, and Sc, in the manufacture of special alloys, laser technology, superconducting compounds, medical-biological and agrochemical preparations, new ceramics, and many other fields. The demand for these elements in the industry of the developed countries of the world has been growing steadily. For example, the demand for vanadium increased from 35,150 tons in 1987 to 65,660 tons in 1990, and at present has already reached the level predicted for the year 2000 (Ivanov, V.V., Borisenko, L.F., Zuyeva, T.I., *et al.*, 1988).

A promising direction for increasing the raw material resources of rare and disseminated elements is the development of nontraditional sources related to heavy and extra-heavy oil, bitumen, and oil shale. Expert estimates indicate huge resources of such rare and disseminated elements as V, Re, Mo, Ni, Se, Cd, Bi, Tl, U, and Ag in oil shale that are much larger than these resources in traditional ores.

Considering the worldwide tendency for an increase in the proportion of heavy oils and, in part, bitumens, both in reserves and in production and refining, the joint development of this raw material, with rare and disseminated elements like V and Ni extracted as by-products, can provide additional reserves of metals in many countries which produce and/or refine metalliferous oil and bitumen. Venezuela alone, in its projected annual production of 87 million tons of heavy oil in the Orinoco belt, can provide half the annual peacetime demand of the countries of the industrial West for vanadium every year by extracting it from petroleum as a by-product. Such oil reserves will last about 500 years, at present rates of production.

Virtually undeveloped rare element resources of Mo, V, Re, U, Se, Cd, Bi, Tl, Ag, Au, Pt, Pd, and others are contained in Phanerozoic black shales, with comparable contents of the metals in the ores of many shale deposits. Comparison of the world's rare element raw material resources of V, Mo, Re, Se, Cd, and Tl in traditional ores with those in black shales shows that the latter contain ten to a hundred times more.

In addition to increasing the rare element raw material resources from nontraditional sources (heavy oil, bitumen, and shale), by-product extraction of metals can substantially reduce the net cost of other products obtained in refining these fuel sources and solve many ecological problems. In many workable deposits of heavy oil and bitumen, elements such as V, Ni, Zn, and As are present in highly toxic compounds. Refining this raw material and, especially, using the heavy residues as furnace fuel, can lead to contamination of the environment unless measures are taken to remove the metals. This pertains equally to metalliferous shales that are usable as solid fuel, binding material for road paving, cementing material, and the like.

If heavy oil, natural bitumen, and shale oil are to be important sources of rare elements, then the amount and distribution of their reserves in known deposits and their geological occurrence as a guide to undiscovered deposits must be understood. To solve these practical problems in Russia and the former Soviet Union, a broad combination of investigations has been carried out, including (1) testing a large group of heavy oil and bitumen deposits for rare elements in various oil and gas provinces of

the former Soviet Union, for example, the Volga-Urals, Timan-Pechora, North Caspian, West Siberian, and East Siberian; (2) studying the composition and ore specialization of black (oil) shales of the main basins of the former Soviet Union (Olenek, Syr Dar'ya and Upper Amu Dar'ya, Volga, Vychegodskiy, and Timan-Pechora Basins) and Estonia (Baltic Basin); (3) expertly appraising the metal resources in heavy oil, bitumen and oil shale by means of analytical data on the rare and disseminated element composition obtained by emission spectrographic, X-ray spectrographic, X-ray fluorescence, and neutron activation methods; (4) preparing the vanadium reserves in the heavy oils of a number of deposits for commercial development; and (5) ecologically evaluating metalliferous deposits of heavy oil, bitumen, and shale, ascertaining toxic and radioactive elements.

One problem to be solved was ascertaining the trends governing the accumulation of rare and disseminated elements in the oil and natural bitumen of various oil and gas districts as the basis for regional prediction of their metal potential. This meant summarizing and analyzing the large amount of analytical data that had been accumulated on the rare and disseminated element composition of petroleum and bitumen, including data published both at home and abroad. This made it possible to carry out naphthometallogenic regionalization of the oil and gas provinces of the world and to distinguish the types of naphthometallogenic provinces that are promising places to prospect for certain metalliferous deposits of heavy oil and bitumen.

A second problem, related to regional and local prediction, was solved by developing theoretical models of the formation of metalliferous deposits of heavy oil and bitumen and determining the possible paths of concentration of the metals (V, Ni, Mo, *etc.*). The models developed on the basis of standard subjects were checked against all available factual data, which made it possible to confirm the correctness of their use for prediction purposes.

The problem of the metallogeny of petroleum and bitumen is closely related to the problem of the origin of petroleum and, in particular, to the role of sapropelic, highly-carbonaceous formations (black shales) in the generation of metalliferous petroleum. On this level, it was important to correlate the rare and disseminated element composition of petroleum, bitumoids, and rocks rich in organic matter with the conditions leading to mobilization of the ore material, both in the rocks themselves and in the petroleum generated from them, *i.e.*, ultimately to ascertaining the causes producing the original metallic specialization of oil and gas provinces. In addition, the presence of anomalous rare-element contents in black shales of a certain genetic type (domanikites) required special investigations to determine the origin of the ore concentrations in them.

Analysis of the rare and disseminated element composition of petroleum, bitumen, and black shale can also be used to identify petroleum-producing formations and ascertain the conditions of petroleum generation with respect to original composition of the petroleum, maturity of the organic matter and crude oils, and stages of generation. This also permits crude-crude, crude-bitumen, crude-source rock, and bitumen-source rock correlations.

The multilevel nature of the problem, in the face of the limited information on many questions, has precluded my elucidating all facets of the metallogeny of heavy oil, bitumen, and shale with the same degree of completeness, or eliminating the controversy concerning a number of new aspects.

This work is based on the results of my many years of research on the metallogeny of heavy oil, natural bitumen, and shale oil, in the context of the work of VNIGRI (St. Petersburg), including results obtained in field work in exploration areas of East Siberia, the Timan-Pechora basin, the Volga-Urals, and Baltic regions, West Kazakhstan, Central Asia, and the Russian Far East.

Geochemical symbols, definitions of certain terms, and acronyms in common usage in the literature of the former Soviet Union, and used in this book in the text, figures, and tables, are given in Appendix A. Stratigraphic symbols appear in Appendix B and the symbols for the different stages of oil and gas generation are depicted in Appendix C.

1

ORIGIN AND DISTRIBUTION OF BITUMEN AND HEAVY OIL

1.1 PROBLEMS OF CLASSIFICATION OF BITUMEN AND HEAVY OIL

Natural bitumen and heavy oil constitute special groups of petroleum and its derivatives which contain high molecular weight hydrocarbons, heteroatomic compounds, and a whole gamut of rare metals.

In classifications, the boundary between heavy oil and bitumen is drawn by most investigators on the basis of a viscosity of 10,000 mPa·sec, which delimits material that is mobile under formation conditions (petroleum) and material that is not (bitumen). In turn, heavy oil is subdivided into three classes on the basis of density (Byramjee, 1983; Martínez *et al.*, 1984): I, 0.9340 to 0.9659 g/cm^3 (20–15°API); II, 0.9659 to 1.000 g/cm^3 (15–10°API); and III, ≥1.000 g/cm^3 (10°API). According to the unified system of classification of petroleum recommended by the World Petroleum Congress (Willmon, 1987), petroleum with a density of 10–22.3°API is heavy, that with a density of 10°API or less is extra-heavy, and that with a viscosity exceeding 10,000 mPa·sec is natural bitumen. In addition, the density and viscosity parameters of petroleum do not always correlate with one another, which leads to ambiguous classification. Multidimensional regression analysis has shown that among the main characteristics of the composition of petroleum, its resin content has a substantial effect on the closeness of the relationship between viscosity and density. For maximum values of the density of petroleum (0.990–1.000 g/cm^3) and resin contents of 35–40%, the limiting viscosity value is 10,000 mPa·sec (Khalimov *et al.*, 1987). It can be postulated that resins are the main stabilizing components in the colloidal structure of heavy oils and bitumens.

According to Syunyayev (1979), heavy oils and bitumens belong to the so-called structural systems in which intramolecular and intermolecular interactions play an important part. The most stable bonds are those in whose formation a larger number of heteroatomic compounds play a part. Therefore, the parameters reflecting the main features of the constitution and structure of the material should be decisive in the physicochemical classification of bitumens and heavy oils. In particular, those characteristics include the degree of polycondensation of the aromatic components of the heavy fractions of petroleum and bitumen and the ordering of these polycondensed regions in the crystals. As an analytical parameter of the variation in the spatial structure of the material, a structural parameter is used, the aromaticity (f_a) determined by X-ray diffraction. Using a selected and diagnostic collection, the 95% confidence interval (with a probability of 0.95) of variation of concentrations of the resin, asphaltene, and carboid components (R, As, C) was found, and from their functional relationship f_a [R, As, C] the range of variation in the parameter f_a belonging to this class was determined (Table 1.1). From the experimental values of f_a and using Table 1.1, the bitumen class can be determined (data from Z.G. Kaplan).

TABLE 1.1
Aromaticity (f_a) of the classes of petroleum and natural bitumen

Class	f_a
Heavy Oil	0.12 – 0.17
Maltha	0.17 – 0.21
Asphalt	0.21 – 0.27
Asphaltite	0.27 – 0.47
Kerite	0.36 – 0.85
Anthraxolite	0.85 – 1.00

One of the best developed classifications of bitumens, based on their physicochemical properties, is that of Radchenko and Uspenskiy (1979). This scheme is given in Table 1.2, which shows the main parameters used for diagnosing the individual subdivisions of the classification. The boundary separating heavy oil from maltha is established on the basis of an oil-fraction content of 65% by weight.

Kurbskiy (personal communication, 1980) suggested using the coking capacity of petroleum and bitumen as the main classification parameter; it is closely related to other parameters, the density and the content of oils, resins, and asphaltenes (Table 1.3).

As the rheological properties of bitumen depend mainly on the colloidal structure and only slightly on the chemical composition, the boundaries between heavy oil and bitumen in classifications based on physical and chemical parameters in many cases do not correspond. For instance, the maltha of the Orinoco belt in Venezuela, composed of less than 65 percent oil, on the basis of chemical parameters, and having a density of 1.00–1.014 g/cm^3, yields small flows of oil naturally because of the relatively high formation temperature (35–65°C) and the presence of dissolved gas. At the same time, most of the degassed heavy oil of the Permian deposits of the Volga-Urals area (0.960–0.980 g/cm^3), which has a formation temperature of about 8°C, cannot be recovered by the usual well methods. As a rule this crude oil, which contains 66–75 percent oil components, is defined as bitumen. Therefore, to solve practical problems of the boundary of anomalously heavy, highly viscous crude oil and maltha, we probably should assign them to a single type of mineral deposit, natural bitumen, which requires the use of intraformational thermal (steam injection, steam drive, or combustion) or mining (pit, shaft) methods for development (Table 1.4).

In the foreign geological literature, the terms "tar sands," "oil sands," "asphaltic rock," and so on are used to designate this group of natural mineral resources, regardless of the type of rock containing the bitumen (including carbonates).

1.2 ORIGIN AND GENETIC TYPES OF NATURAL BITUMEN

In our previously published monograph "Natural Bitumens of the USSR" (Goldberg, 1981), we examined the main processes of bitumen genesis which lead to the formation of the entire known range of natural bitumens (Table 1.5). This genetic classification of natural bitumens is included in the "Dictionary of Oil and Gas Geology" (Chernikov, 1988).

The nature and direction of the processes of formation and transformation of hydrocarbon fluids determine not only the geochemical type of heavy oil and bitumen, but also the distribution and level of concentration of metals in them. Therefore the scheme of bitumen genesis considered below is directly related to the problem of the metallogeny of heavy oil and bitumen.

The Supergene Series of Natural Bitumens

The vast majority of heavy oil and bitumen accumulations known in the world are concentrated in the supergene zone, the lower boundary of which is situated at an average depth of 1800–2000 m. However, this boundary may vary, depending on the geologic and hydrogeologic features of a given basin, the geothermal gradient, and the duration of existence of the hydrocarbon accumulations in the ground. Oxidation of petroleum in the supergene zone occurs in several stages and under the influence of various factors. In the early stages in the cryptosupergene zone, the main role is played by biogenic

TABLE 1.2
Classification of natural bitumen based upon physicochemical properties [after Radchenko and Uspenskiy, 1979]

Class, subclass		Consistency	Solubility in chloroform (%)	Density (g/cm^3)	Behavior when heated (°C)	Yield of volatiles (% of OM)	Optical parameters	Typical elemental composition (%)
Maltha		Viscous & viscous–liquid	100	0.96 – 1.00	Melts easily	–	–	–
Asphalt		Viscous to solid	100	about 1.00	$T_M < 100$	–	–	–
Asphaltite	Gilsonite	Solid	100	1.05 – 1.15	$T_M = 100 – 200$	70 – 90	Rm = 0.01 – 0.17 n = 1.60 – 1.64	H = 9 – 10
	Grahamite	Solid	90 – 100	1.15 – 1.20		50 – 70	Rm = 0.4 – 0.8 n = 1.60	H = 7.5 – 8.5
Kerite	Albertite	Solid	10 – 20	1.07 – 1.10		50 – 75	Rm = 0.15 – 0.80 n = 1.66 – 1.69	C = 80 H = 9
	Impsonite	Solid	10	1.10 – 1.25		10 – 50	Rm = 0.8 – 3.5 Rb = 5 – 11	C > 90 H ~ 5
Anthraxolite	Low	Solid	Insoluble	1.30 – 1.40	Burns slowly without flame	< 10	Rm = 1.8 – 2.1	C = 88 – 93; H = 3 – 5
	Medium			1.40 – 1.70			Rm = 3 – 6.5	C = 93 – 97; H = 1 – 3
	High			1.80 – 2.00			Rm = 4 – 7	C = 96 – 99; H = 1
Oxykerite		Solid and unconsolidated	Incomplete	1.15 – 1.25	Blisters when melted	–	–	H = 6 – 7 O ≥ 5 – 6
Huminokerite		Unconsolidated	Insoluble	1.25 – 1.50	Blisters or carbonizes without caking	–	–	H = 4 – 6.5 O ~ 30
Ozokerite		Solid and waxy	100	0.91 – 0.97	$T_M = 35 – 100$	to 100	Rm < 0.01 – 0.05	C = 84.5 – 86 H = 13.7–15.3
Elaterite		Solid	Weak	1.00 – 1.10	Softens and decomposes	–	–	C = 75 – 77 H = 11 – 12
Wurtzilite		Solid	<10	1.05–1.07	Softens and decomposes	75 – 95	Rm = 0.02 – 0.15 n ~ 1.51 – 1.59	H = 10 – 12 S ≥ 3.0

TABLE 1.3
Classification of petroleum and natural bitumen based upon coking capacity [Kurbskiy, personal comm., 1980]

Class	Coking capacity (%)	Density (g/cm^3)	Total resins plus asphaltenes (wt%)	Asphaltene content (wt%)
Conventional petroleum	<8	<0.91	10 – 20	Up to 5 – 6
Heavy oil	8 – 12	0.91 – 0.98	21 – 35	4 – 10
Maltha	13 – 25	0.98 – 1.03	35 – 60	10 – 25
Asphalt, asphaltite	>25	>1.03	60 – 98	>25

oxidation (biodegradation) of petroleum, loss of a substantial part of the *n*-alkanes, and their transformation into petroleum with a more cyclic hydrocarbon composition. These changes are accompanied by loss of up to 20 percent of the oils in naphthene and methanenaphthene petroleum, and up to 50 percent of oils in methane petroleum with a high content of *n*-alkanes. The order of consumption of petroleum hydrocarbons by bacteria takes place, in general form, according to the following scheme: first the *n*-alkanes lighter than C_{25}, monocyclic cyclanes, and isoprene alkanes are destroyed, followed by the aromatic compounds. Intensive lateral migration of infiltrating waters promotes the biogenic oxidation of petroleum; this is manifested in the marginal parts of some oil and gas basins adjacent to outcrops of crystalline shields or large eroded arches.

When infiltrating waters containing metal ions, particularly vanadium ions, react with petroleum, they may be enriched in those elements (see Chapter 3.4).

Under near-surface conditions, in idiosupergene zones, when free oxygen is introduced, chemical transformation of high-molecular-weight compounds occurs, in addition to further microbial (aerobic) oxidation, according to the scheme:

$$MCAr \rightleftharpoons BCAr \rightarrow PCAr \rightarrow RB \rightarrow RAB \rightarrow As \rightarrow C$$

In the formation of new asphaltic and resinous substances at the expense of high-molecular-weight arenes containing virtually no heavy metals (V, Ni, Mo, Cr, *etc.*), there is no enrichment of the asphaltenes and resins in these elements. Relative accumulation of metals in such oxidized heavy oil is related only to physical weathering processes, evaporation of light fractions and water washing, which lead to residual accumulations of metalliferous resin and sulfur compounds.

Enrichment of petroleum in sulfur promotes an increase in its density and viscosity. There are differing points of view concerning the nature of the sulfur compounds in crude oil. Most investigators hold to the idea that the addition of sulfur to oil occurs in pools and is derived from agents such as hydrogen sulfide, formed in biochemical and thermochemical reduction of sulfates by formation waters, and native sulfur. Sulfur reacts very readily with polycyclic aromatic hydrocarbons; carbonate rocks, acting as catalysts, greatly influence the reactivity of hydrocarbons. Some investigators (Tissot and Welte, 1978; Botneva, Yeremenko, Maksimov *et al.*, 1985) believe that high-sulfur petroleum is genetically related to sulfur enrichment of the parent rocks by organic matter. In the opinion of these investigators, if carbonate and clastic sediments contain the same kind of organic matter, the carbonate

TABLE 1.4
Classification of heavy oil and natural bitumen based upon method of development

Type of mineral deposit	Group of natural bitumens and petroleum	Consistency	Density (g/cm^3)	Viscosity (mPa·sec)	Total resins plus asphaltenes (wt%)	Method of development
Petroleum	Heavy oil	Liquid	0.934 - 0.965	150 – 1000	<25	In situ
	Extra-heavy	Viscous-plastic, slightly fluid, and viscous (thermoplastic)	0.965 – 1.036	1000 – 100,000	25 – 60	Intraformational or mining
Bitumen	Asphalt, asphaltite	Solid, less often viscous (thermoplastic)	1.036 – 1.20	>100,000	>60	Mining

parent sediments will produce crude oil containing more sulfur, *i.e.*, there are no metal ions capable of removing hydrogen sulfide from the sphere of the reactions and binding it in metal sulfides. The question of the nature of the sulfur in oil is extremely important for understanding the conditions of accumulation of some metals in petroleum, particularly vanadium, as well as of metalloporphyrins.

Available data indicate that two processes of sulfur accumulation in petroleum exist in nature, secondary sulfur of the supergene and paleosupergene type, and original sulfur-bearing oil of the so-called "immature" type. In connection with the specifics of formation of such heavy oils from the organic matter of immature parent rocks indicated by the level of catagenesis not greater than MK and vitrinite reflectance of not less than 0.60% Ro, they are enriched in high molecular weight and heteroatomic compounds, which predetermines their relatively high metal content. In those cases where the source of the "immature" heavy oil is metalliferous domanikites, the petroleum contains high concentrations of vanadyl porphyrins, vanadium, and other heavy metals, as, for example, in the Early Carboniferous petroleum of the Melekess Basin and the Miocene and Oligocene-Miocene petroleum of the Santa Maria, Ventura, and Santa Barbara Channel Basins. Typical of such petroleum is a predominance of alkanes in the light fractions (low boiling point: <130°C) and a rather low content of cyclanes and arenes. In the fractions boiling above 200°C, the amount of arenes increases sharply and the proportion of cyclanes decreases relative to the ratio of normal and isoalkanes, the values of the coefficient of metamorphism, the ratio of alkanes to cyclanes, and other indices. Such petroleum has not undergone substantial catagenic alteration (Shimanskiy, Tsyrkina, and Vasil'yeva, 1973; Chakhmakhchev, 1983).

Among the metalliferous components of "immature" heavy oil, asphaltenes, whose concentration amounts to 5–18 percent, resins (15–40 percent), and sulfur (2–5 percent) play a definitive role. From the example of the heavy oil of the Melekess Basin, Lazareva and Aksenova (1986) found that all the fractions of such petroleum are enriched in sulfur, the amount of which increases systematically as the boiling point increases. Organic sulfur compounds have a low threshold of thermal stability, about 100°C, and consist mainly of sulfide sulfur (35–53 percent) and residual sulfur (45–62 percent).

Physical weathering processes play a large part in the alteration of petroleum in the supergene zone. In some cases they prevail over the processes of oxidation of the petroleum. As an example, consider the results of a study by the VNIGRI of heavy vanadium-bearing petroleum from the Cerro Negro field in Venezuela, a sample of which we obtained from the plant at Morichal. Results of analysis of the crude are given in Table 1.6. The data obtained show that despite the high density (1.0117°API), the crude is only very slightly biodegraded. This is indicated by the following: (1) predominance of benzene-soluble over alcohol-benzene-soluble resins ($R_B/R_{AB} = 1.8$); (2) low proportion of asphaltenes in the composition of the asphaltene-resin components ($A/(A+R) = 0.3$); (3) predominance of aromatic and mixed structures over methane structures in the crudes ($Me–Nf)/\sum Ar = 0.5$); (4) prevalence of monoaromatic over polyaromatic structures ($Ar_I/Ar_{III} = 1$; $Ar_I/(Ar_I–Ar_{III} = 0.9$). The composition of the aromatic fractions of the petroleum, determined by electron spectral absorption, showed that they contain benzene (66.6 percent), naphthalene (16.1 percent), phenanthrene (9.1 percent), chrysin (3.1 percent), benzanthracene and benzphenanthrene (3.3 percent), and pyrene (1.8 percent) hydrocarbons. The concentration ratios of the aromatic carbon contained in the naphthalene hydrocarbons and polycyclic arenes ($C_{naphtha}/C_{PAr} = 1.1$) confirms that this oil is not very oxidized.

Investigation of the composition of aromatic hydrocarbons in the entire genetic series of petroleum heavy oil – maltha – asphalt – asphaltite makes it possible to show the trend of the processes of transformation of petroleum and the genetic type of heavy oil and bitumen (Temyanko, Solov'yeva, and

TABLE 1.5
Genetic classification of natural bitumen [from Goldberg, 1981]

Process	Original substance	Groups, classes subclasses	Density (g/cm^3)	Parameters of group & hydrocarbon composition (%)	Other typical parameters
Supergene (oxidized) series of natural bitumens					
Biochemical oxidation, evaporation of light fractions	Petroleum	Extra–heavy oils Malthas Asphalts	0.965 – 1.00 0.975 – 1.03 1.03 – 1.10	75 – 65 65 – 40 40 – 25	– – –
Chemical oxidation, residual accumulation of tar and sulfur	Cyclic hydrocarbons, resins, petroleum	Malthas Asphalts Asphaltites	0.965 – 1.03 1.03 – 1.10 1.10 – 1.20	65 – 40 40 – 25 <25	R_{AB} = < 1.1 (Me + Nf)/Ar < 1.2
	Methane and naphthene low–resin petroleum	Kirs (malthas, asphalts, asphaltites)	0.965 – 1.20	<65	R_{AB}/R_B = > 1.3 (Me + Nf)/Ar > 1.8
Intensive chemical oxidation under subaerial conditions	Asphaltic bitumens	Ozokerites Huminokerites	1.15–1.25 1.25–1.50	<5 –	K = 10 – 40% K = 40 – 100%
Intensive bacterial oxidation	Paraffinic bitumens	Algarites Elaterites	~1.00 1.0–1.10	– –	– –
Phase–migration series of natural bitumens					
Natural deasphaltization of petroleum by gas or light paraffin hydrocarbons	Petroleum relatively rich in asphaltic resinous substances	Asphaltites, (asphalts, asphaltites, kerites)	>1.10	<40	A/T = 2 – 4
Concentration of asphaltic resinous substances during migration as a result of disruption of equilibrium state in colloidal system of petroleum (vein bitumens)	Heavy resinous oils, viscous malthas	Asphalts Asphaltites Lower kerites	~1.10 1.10 – 1.15 >1.15	40 – 25 <25 <5	Parameters similar to those of asphaltenites

Table 1.5 cont'd ...

Process	Original substance	Groups, classes subclasses	Density (g/cm^3)	Parameters of group & hydrocarbon composition (%)	Other typical parameters
Phase–migration series of natural bitumens (continued)					
Differentiation of gas condensates and high-paraffin petroleum during migration, leading to accumulation of solid paraffins	Heavy gas condensates and paraffin petroleum	Ozokerites	0.85 – 097	45 – 95	$C_{37}H_{78} - C_{53}H_{108}$
Thermal–metamorphic series of natural bitumens					
Hydrothermal differentiation during migration in hot solutions	Paraffinic petroleum Resinous petroleum	Hatchettites Kerites Lower anthraxolites	0.86 – 0.94 1.07 – 1.25 1.30 – 140	~100 <5	$C_{21}H_{44} - C_{38}H_{73}$ K = 10 – 95% K = 95 – 100%
Predominance of petroleum bitumens under conditions of contact, hydrothermal, regional, and dynamic metamorphism	Asphaltic bitumens and heavy, highly resinous oils	Kerites Albertite Impsonite Anthraxolites Lower Medium Higher Petroleum coke	 1.07 – 1.15 1.10 – 1.25 1.30 – 1.40 1.40 – 1.70 1.80 – 2.00 >1.70	 5 – – – –	 K = 10 – 95% K = 95 – 100% K = 100%
Destruction of organic matter under conditions of contact metamorphism with the formation of a broad spectrum of of bitumens (naphthoids)	Oil shale, coal and other rocks rich in organic matter	Asphaltic bitumens of all classes (α–naphthoids) Chyrsmatite Olefinite Others	Parameters similar to parameters of bitumens of petroleum series (naphthides) <1.00 0.95 – 1.15 1.20 – 1.30 1.40	 100 – – –	 – – $C_{24}H_{18}O$ $C_{32}H_{17}O$

TABLE 1.6

Elemental and hydrocarbon group composition of heavy oil from Cerro Negro Field, Venezuela [Source: VNIGRI data]

Elemental composition (%)					Group composition (%)				Group composition (fraction, %)					Hydrocarbon group composition (%)			
C	H	N	S	O	Oily fraction	R_B	R_{AB}	A	Me-Nf	I-Ar	II-Ar	III-Ar	Loss	Me-Nf	I-Ar	II-Ar	III-Ar
81.81	9.03	0.53	3.10	5.35	41.92	27.11	15.16	15.8	35.13	28.62	13.59	21.82	0.84	35.42	28.86	13.72	22.0

[Note: Oily fraction: hydrocarbons heavier than C_3]

Goldberg, 1985). It was found that for "normal" crude in the zone of catagenesis, the concentration distribution of the main groups of condensed hydrocarbons has the form naphthalenes → phenanthrenes → chrysenes → benzanthracenes → pyrenes. That distribution is retained for methane and methanenaphthene petroleum under the conditions set for the model experiments on their biodegradation.

For heavy oil, maltha and asphalt of the supergene and paleosupergene types, the distribution of condensed hydrocarbons has a different form: phenanthrenes → naphthalenes → chrysenes.

Under the conditions of subaerial weathering, petroleum is further oxidized, with the formation of a whole gamut of bitumens of the supergene series (Table 1.5). Crude oils of different composition form different groups of bitumens. In the alteration of methane and naphthene petroleum, bitumens of the kir group are formed; they are enriched in oxygen and depleted in nitrogen, alcohol-benzene-soluble resins predominate over benzene-soluble resins, and chiefly methanenaphthene hydrocarbons are present in the oil fraction. As a rule, kir does not contain elevated concentrations of V, Ni, Mo, Cr, and other heavy metals. In rare cases, secondary enrichment of kir in other elements is observed. Various forms of accumulation of bitumens are typical of kir, from sheetlike to stratiform deposits, sometimes containing large reserves (the deposits of western Kazakhstan). Kir deposits are most widespread in regions underlain by Mesozoic-Cenozoic deposits (North Caspian, South Caspian and North Caucasus-Mangyshlak Provinces in the former Soviet Union), which contain slightly resinous naphthenic petroleum with low concentrations of asphaltene components in the upper horizons.

The products of similar transformations of crude oils that are more cyclic and richer in asphalt-resin components are typical malthas, asphalts, and asphaltites, which have relatively neutral resinous substances and a relatively high content of aromatic hydrocarbons in the oil fraction. As a rule, these bitumens are enriched in heavy metals (V, Ni, Mo, Cr, *etc.*), of which vanadium and nickel have the highest concentration. In some bitumen deposits these metals may be of economic importance. The main regions where normal asphalt bitumens of the supergene type occur are old cratons as well as the systems rimming them.

As a result of intensive chemical oxidation under subaerial conditions, asphaltic bitumens of various genetic lines convert to varieties that are soluble or insoluble in organic solvents: oxykerites and their high-sulfur varieties (thiokerites), and huminokerites. Parageneses of these bitumens with uranium minerals are of great interest. It is well known that petroleum is capable of extracting uranium from infiltrating waters or from the host rocks. However, in the series of petroleum → heavy oil → maltha → asphalt, uranium never forms economic concentrations. Only in the next stages of transformation of bitumens (in the case of intensive oxidation or metamorphism) can the amount of uranium reach economic concentrations due to its accumulation in carboids and carboxyl compounds. In some oxykerites and huminokerites, the uranium content reaches tens of percent.

For bitumens of the supergene type, a general tendency is observed toward a decrease in the extent of their variability and an increase in their concentration from older to younger deposits. This apparently reflects the cyclic character of the formation and destruction of oil pools.

Supergene bitumens constitute the vast majority of the products of transformation of primary petroleum. All the very large and giant concentrations of bitumens known in the world are of supergene origin.

The Phase-Migration Series of Natural Bitumens

This series consists of three genetic lines of bitumens. The first genetic line — from asphalts to low anthraxolites — is related to processes of natural deasphaltening of crude oil in the pool. These bitumens, which we call asphaltenites, are fairly common in the oil, gas, and gas-condensate pools of the Timan-Pechora, Volga-Urals, North Caspian, and East Siberian Basins in the former Soviet Union, the Baltic Basin in Estonia, and the Western Canada Sedimentary Basin.

Goldberg (1973, 1978, 1981) believes that deposition of asphaltenite in producing formations is the result of the introduction of light oil or gas into a concentration of more or less heavy oils enriched in asphalt-resin components. In this case the character of the precipitated bitumen and its concentration in the rocks will depend on the ratio of the volumes of primary petroleum and newly arriving fluid, as well as on the details of their chemical composition. Asphaltenite forms stratiform and lenticular accumulations in producing formations, sometimes reaching a thickness of more than than 10 m (Usa and Vozey deposits in the Timan-Pechora Province and the Tengiz and Karachagan deposits in the North Caspian Province). Laboratory and artificial processes of deasphaltening of petroleum were taken as a model of the formation of the natural bitumens of this series (Goldberg, 1978). Comparison of asphaltenites and artificial asphaltites obtained in deasphaltening of petroleum by the "Doben" process showed that their chemical and spectroscopic characteristics were similar. A higher content of asphaltenes (for instance, up to 55 percent for asphalt), a predominance of asphaltenes over resins (A/R = 2 to 4), and relatively high contents of C, H, and N, with low percentages of oxygen and asphaltogenic acids, distinguish the asphaltenite group from supergene bitumens. These features of the chemical composition and the conditions of formation of asphaltenite should predetermine their relatively high metal content. To a certain extent this is confirmed by the results of analysis of artificial asphaltites obtained in the deasphaltening of crude oil. For instance, artificial asphaltite from the Samotlor petroleum contains more than 3000 ppm vanadium and nickel in the ash, and asphaltite from Romashkino crude contains more than 3000 g/t of vanadium and 1300 g/t of nickel. Study of the products of deasphaltening of a number of crude oil samples sent to VNIGRI by the French Petroleum Institute showed that the content of metals (V, Ni) in the residues of deasphaltened oil is 5 to 10 times higher than their content in the original petroleum.

The second genetic line of bitumens (asphalts, asphaltites, lower kerites) in the phase-migration series is related to differentiation, during migration, of heavy oils and liquid malthas rich in asphalt-like components (asphaltenes, resins, sulfur compounds), leading to the formation of accumulations of vein bitumens. In a general way, the geochemical aspect of the formation of these bitumens consists of a process leading to concentration of asphalt-resin components due to disruption of the equilibrium state in the colloidal system of the moving petroleum. As the reason for this phenomenon, the following processes can be considered:

1. Abrupt cooling of petroleum arriving in a fracture due to adiabatic expansion of gases liberated from it, which would lead to separation (coagulation) of the asphalt-resin components;
2. Reduction in viscosity of the petroleum due to its multiple dilution by gaseous and light liquid hydrocarbons, in the case in which a fracture simultaneously penetrates pools of different composition and phase state. This causes deposition of asphaltenes and other high molecular weight compounds in the fracture in a way analogous to the process of natural deasphaltening of petroleum in pools;

3. Chemical and physical processes leading to loss of light components, removal of petroleum components, and residual accumulation in fractures, of the heaviest resin-asphaltene part of the petroleum, which later was subjected to water-washing and biodegradation.

The presence of relatively high sulfur concentrations in the original heavy oil apparently promotes polymerization and condensation of the most reactive substances and the formation of high molecular weight compounds. Actually, high-sulfur varieties predominate in very large accumulations of vein bitumens, for example, in the Sadki asphaltite (7.3 percent S), Kairovo asphaltite (7.0 percent S), Ivanovskoye asphaltite (up to 7.7 percent S), and bitumens of the vein system of southeastern Turkey (5.4–9.0 percent S).

The final stage of formation ("prematuration") of these bitumens takes place when the fracture is compressed, causing the liquid and gaseous components to be expressed and the viscous mass to be compacted.

The accumulation of ore concentrations of V, Ni, Mo, and Re, and less often Ag, Au, As, Sb, and Cd is related to vein bitumens; this results from the physical concentration of metalliferous components, the asphaltenes, resins, and sulfur compounds of the original heavy oils. Some deposits of vein bitumen contain economic concentrations of vanadium, nickel, and other elements (see Chapter 4).

The third genetic line in the phase-migration series is related to differentiation of gas-condensate mixtures during migration and, as a result of phase-retrograde processes, the formation of ozokerites from the highly paraffinic crude and heavy paraffinic bitumens. It has been demonstrated theoretically that as a result of a reduction in pressure and temperature to below critical values, the liquid phase separates out of the gas-condensate mixture, *i.e.*, a retrograde condensation effect is observed (Starobinets, 1974). The separation of hydrocarbons from gaseous solution takes place in the reverse order of their solubility, which leads to accumulation of the highest-molecular-weight components in the liquid phase, depleting it in the low-boiling fractions, which go off into the gas phase. The boiling point of typical retrograde petroleum is often considerably raised, in the face of a reduced content of the benzene fractions, even in the relatively light fractions. As solid hydrocarbons are concentrated chiefly in the fractions that boil above 300°C, the formation of highly paraffinic petroleum of such origin is possible only at the expense of heavy condensates migrating from greater depths. Our earlier calculations (Goldberg, 1981) showed that the amount of solid paraffin that can find its way from gas condensate into the liquid phase is quite comparable to analytical data on the paraffin content, that is, of chiefly gas-condensate origin, in the crude oil in many fields.

Despite the widespread occurrence of high-paraffin petroleum, which can be considered the potential source, ozokerite accumulations are rather rare, especially on a commercial scale (western Turkmenia, the Carpathian region, and Fergana). A necessary condition for ozokerite formation is the presence of faults that penetrate pools of heavy gas condensate or highly paraffinic crude oil and emerge at the surface.

The physical conditions for ozokerite formation derive from retrograde condensation of gas condensate, in conjunction with strong cooling due to adiabatic expansion of gases, which leads to "freezing" of even the low fractions of ozokerite and subsequent removal of the solution from the sphere of ozokerite formation. The scale of ozokerite accumulations obviously depends to a considerable extent on the duration of introduction of the ozokerite-forming fluid and the capacity of the host-rock zones.

Ozokerite is a mixture of solid hydrocarbons, liquid oils, and resinous substances. It is very unstable. Solid paraffins, which constitute the main mass of ozokerite, are easily subjected to bacterial

decomposition, which converts them to algaritic varieties which are a mixture of hydrocarbons and proteins. Therefore, fairly large deposits of ozokerite are known only in young deposits no older than Paleogene.

In connection with the conditions of its formation and composition, ozokerite contains virtually no heavy metals (V, Mo, Cr, and Co). Only enrichment of highly paraffinic petroleum, accompanied by ozokerite, with elements such as Hg, Sb, and Cd, introduced into the petroleum with gaseous emanations, is possible.

The Thermal-Metamorphic Series of Natural Bitumens

This series consists of carbonized varieties, from kerite to petroleum coke, and paraffin minerals (Table 1.5). On the basis of the conditions of manifestation of thermal-metamorphic processes and the nature of the original material, several genetic lines of bitumens are distinguished (Goldberg, 1981):

1. Kerite → anthraxolite → petroleum coke, related to the contact effect of intrusions and hot springs on previously-formed accumulations of asphaltic bitumens or resinous oils;
2. Hatchettite, kerite, and anthraxolite related to hydrothermal differentiation and metamorphism under conditions in which petroleum is transported by hot solutions;
3. A broad spectrum of bitumens (naphthides) formed in the destruction of organic matter (oil shales, coal, *etc.*) under conditions of contact metamorphism. The main regions of occurrence of bitumens of this series are folded mountains and sedimentary basins with extensive manifestations of magmatic activity, such as the Tungusska in the former Soviet Union, Parana in Argentina, Brazil, and Paraguay, Karroo in South Africa, and Morondava in Madagascar.

Bitumens of the first genetic line, which may contain a broad spectrum of rare elements (V, Mo, U, Au, Hg, Sc, Ag, *etc.*), are of most interest with respect to metal potential. Accumulation of these metals in bitumens is related to endogene introduction of material and deposition at redox barriers. Despite the relatively small scale of accumulations of these heavy bitumens, the extremely high concentration of some metals in them, especially vanadium and uranium, makes them objects of potential economic production of the metals. According to Parnell (1988), bitumens with exceptionally high contents of uranium or vanadium contain these metals in the form of inorganic material, uraninite and vanadium-sulfide natronite, which separate out of bitumen during its alteration, losing their bonds to organic complexes. The highly vanadiferous bitumen-natronite veins in Peru and Argentina are also enriched in nickel, and those in Colombia contain high concentrations of molybdenum (up to 1000 g/t).

Bitumens from some ore deposits in Britain contain uranium concentrations of up to a few percent, at which level the uranium occurs in the form of mineral inclusions (Parnell, 1988). The uranium-bitumen deposits of the Colorado plateau are widely known, as are the hydrothermal uranium-bitumen deposits in the former Soviet Union, with a high concentration of uranium. A unique type of uranium-thorium bitumen is thucholite, found in the United States, Sweden, South Africa, and other places. Thucholite often contains high concentrations of gold and platinum-group elements.

The observed paragenesis of many ore elements with bitumens in hydrothermal and contact-metasomatic deposits is not always interpreted unequivocally; a number of investigators consider these finds to be evidence of the endogene origin not only of the metals, but also of their host bitumens. However, in many examples of this type that we have studied, a spatial rather than a genetic

relationship of the bitumens to the metals is fairly definitely established, in connection with their common paths of migration along fault zones.

1.3 GEOLOGIC DISTRIBUTION OF BITUMEN AND EXTRA-HEAVY OIL DEPOSITS

The genetic and spatial relationship of bitumens and extra-heavy oils, and all very large accumulations of them, to oil and gas basins enables us to consider the basin as the main unit of bitumen-geological regionalization. Such basins comprise an association of neighboring oil-and-gas and bitumen districts. The differences between districts is determined by the details of their tectonic evolution and structure at the stages that ended cycles of oil and gas accumulation. The largest deposits of bitumen and extra-heavy oil occupy the so-called aconservation zones of present oil and gas basins; such basin-margin zones usually contain less than 500 m of sedimentary rocks and are essentially devoid of commercial petroleum accumulations. The percentage of the total amount of hydrocarbons represented by bitumens and extra-heavy oils that originally accumulated in a basin depends on the intensity of whatever processes promoted the destruction of the pools. This could be caused by any of the following factors.

1. Intensive uplift of large oil- and gas-bearing territories (or individual elements of them) and emergence of the oil pools formed in them into the supergene or paleosupergene zone.
2. Development of zones or paleo-zones of infiltration of fresh and not very mineralized oxygenated waters both laterally (chiefly from the rim of the basin), and vertically (in connection with deep erosion and other exogene processes).
3. Introduction of petroleum into the peripheral zones of basins where the cover is thin and there are no effective caprocks.
4. Extensive manifestation of fault tectonics, salt diapirism, and mud volcanism, or the formation of other paths allowing hydrocarbons to escape from traps, all the way to seepage of petroleum at the surface (present or old).
5. An abrupt increase in degree of metamorphism and deformation of deposits that previously were petroliferous, such as is manifested by intensive magmatism.

The scale of concentration of bitumens and extra-heavy petroleum in oil and gas basins depends on the intensity of whatever processes are capable of destroying oil pools. The loss of petroleum in a basin, or in an individual part of one, can be determined from the formula:

$$Q_{ol} = \frac{Q_b \cdot K_m}{Q_b \cdot K_m + Q_o} 100\% ,$$

where Q_{ol} is the amount of crude oil lost, Q_b is the resources of bitumen and extra-heavy oil, K_m is the coefficient of loss of mass of crude oil, which depends on the extent of transformation of the bitumens, and Q_o is the potential petroleum resource.

The basins of old cratons, including the East Siberian, Russian, and North American, and those associated with Mesozoic-Cenozoic marginal and foreland depressions like the Western Canada, Eastern Venezuela, and Lena-Anabar Basins, have the greatest loss.

For basins of a different type, we earlier calculated (Goldberg, 1981) the approximate values of the loss of petroleum in bitumen formation and reconstructed the original oil reserves that the basins contained, up to the stage or stages of their destruction. For instance, in the Western Canada Sedimentary Basin, the coefficient of oil loss is 0.95–0.98; in the Lena-Anabar, 0.65; in the Volga-Urals, 0.35–0.40, and in Timan-Pechora Province, 0.25–0.30.

The maximum value of petroleum resources for various oil-and-gas basins falls in certain stages. For instance, the East Siberian Basin contained its maximum concentration in the early-middle Paleozoic stage and the Timan-Pechora Basin in the late Paleozoic-early Mesozoic stage. For basins of equal scale and of the same tectonic type, the potential reserves of hydrocarbon fluids and natural bitumens are determined comparably, for instance, the Western Canada and Eastern Venezuela Basins and the basins of the Persian Gulf.

On the basis of the richness in reserves of bitumens and extra-heavy oils, the oil-and-gas basins of the world are arranged according to the following tectonic types:

1. basins of marginal depressions at the junction of old cratons and young folded mountains;
2. basins of old cratons;
3. basins of epicratonic intermontane depressions;
4. basins of perioceanic depressions.

They are lumped together into groups of basins of cratonic regions, marginal systems, and mobile belts.

Cratonic Regions

In the territory of the former Soviet Union, cratonic oil and gas basins containing fairly large accumulations of bitumens and extra-heavy oil include the East Siberian, Timan-Pechora, Volga-Urals, North Caspian, and South Mangyshlak. Cratonic basins abroad include the Illinois Basin in the United States, the Morondava Basin in Madagascar, and the Lower Niger Basin in Nigeria.

Summing up the data on the characteristics of the bitumen potential of the above basins (Goldberg, 1981), the following points can be mentioned:

1. The main resources of bitumen and extra-heavy oil are in the basins of old cratons, characterized by petroleum accumulations in relatively early stages of evolution (P_{z1} on the Siberian craton; C_3, P_1, and P_2 in the Timan-Pechora Basin, and T in the Volga-Urals Basin), which subsequently evolved with a predominance of rising tectonic movements.
2. In each basin, the main bitumen and extra-heavy oil resources are confined to relatively narrow stratigraphic intervals (Vendian-Lower Cambrian Series on the Siberian craton, the Viséan stage in the Timan-Pechora Basin, and the Permian deposits in the Volga-Urals Basin), although the range of occurrence of bitumens usually encompasses almost the whole section of the sedimentary cover.
3. Districts and zones of bitumen accumulation are controlled by certain elements of the structural position and tectonic evolution: (a) eroded arch and paleo-arch uplifts on old cratons (Anabar and Olenek arches on the Siberian craton; Central Pechora, Omra-Soyvapaleo uplift; and "Zinchenko" paleo-arch in the Timan-Pechora Basin); (b) junction zones between intra-cratonic

Paleozoic basins and arches contrastingly developed in Mesozoic-Cenozoic and Recent time (conjugate slopes of basins and arches on the Russian craton); (c) monoclinal margins of large basins on old cratons in aconservation zones of basins (marginal zones of the Illinois and Western Interior basins of the North American craton and the Congo syneclise of the African craton); (d) large zones of uplift on young and on reactivated old cratons with Cenozoic and Recent stages of uplift (Central Emba zone of the North Caspian Basin and the Beke-Bashkuduk and Tyub-Karagan rises of the South Mangyshlak Basin; (e) rift zones (Dead Sea graben, Baikal rift, and the Rhine graben; and (f) monoclinal edges of perioceanic basins adjacent to the shields of old cratons (Morondava, Lower Niger, and Cuanza-Cameroon Basins on the edges of the African craton).

4. Asphaltic bitumens and highly resinous heavy oils are predominantly developed in cratonic basins; ozokerites are mainly typical of rift zones. According to our estimates, the basins of old cratons contain 7–8 percent of the world's natural bitumen resources.

Marginal Systems

The main bitumen and extra-heavy oil resources are related to oil-and-gas basins of marginal and foreland depressions. On the basis of scale and conditions of concentration of natural bitumens, these basins fall into two groups:

1. Basins of marginal and foreland depressions at the junction between old cratons and young folded mountains (Western Canada, Eastern Venezuela, Barinas-Apure, and Lena-Anabar Basins, and the Verkhoyansk area).
2. Basins of marginal depressions at the junction between cratons with folded mountains of the same age (Cis-Ural, West Kuban, and Terek-Caspian Basins).

The first group of basins contains bitumen and heavy oil deposits on its monoclinal outer edges, adjacent to shields and arches of old cratons. At least 85 percent of the potential world resources of bitumen and heavy oil are concentrated in just two basins of this type, the Western Canada and Eastern Venezuela.

From the periphery to the center of these basins, a gradual change may be observed from deposits of bitumen to deposits of extra-heavy oil, heavy oil, and then light oil. In the zones of junction between Mesozoic-Cenozoic marginal depressions and negative structures of old cratons, bitumen concentrations are not usually formed. Sheet and fracture deposits of bitumen are typical of the intensively dislocated interior zones of these basins; on the whole they contain relatively small reserves (hundreds of millions of tons). In addition to asphaltic bitumens, ozokerite deposits have been found in these zones (Pokutsk-Borislav and other zones of the Cis-Carpathian depression).

The bitumen potential of the second group of basins is limited mainly to narrow local zones in which the oil pools have been destroyed. These zones are related to fault dislocations, mud volcanoes, salt and gypsum diapirs, and deeply eroded structures in which oil-bearing formations crop out at the surface. In marginal depressions of the Alpides (West Kuban, Terek-Caspian), the bitumens consist chiefly of malthas (highly resinous oils); in Hercynian depressions (Cis-Ural, Cis-Appalachian, *etc.*) the bitumens are mainly asphalt and asphaltite. The bitumen reserves in these basins are very limited.

Mobile Belts

In orogenic regions, accumulations of natural bitumens are exceedingly diverse in structure, composition, and scale of concentration. They are found in many oil-and-gas basins related to epi-geosynclinal intermontane and interior depressions (Kura, Apsheron-Kobystan, West Turkmenian, Adriatic); epicratonic basins(Fergana, Uinta-Piceance); synclinorium depressions (Khatyr, Santa Maria); and in zones consisting of a folded complex and a basement complex.

The determining factors in the localization of natural bitumens in basins of epi-geosynclinal and interior depressions are the development of faults and mud volcanoes in oil and gas structures and active erosion of the latter, exposing oil-bearing formations in the supergene zone. This produces the chief occurrence of sheet and vein deposits of bitumens within the boundaries of oil-and-gas structures. For instance, the Cheleken Field in the West Turkmenian depression and the Balakhany-Sabunchi-Ramani and Binagadi Fields in the Apsheron-Kobystan depression often contain such deposits of heavy, degassed oil in the upper horizons.

The basins of epicratonic intermontane depressions, on the whole,contain more substantial reserves of bitumens than epi-geosynclinal depressions, the increase in the level of bitumen content in them being due to pre-orogenic (cratonic) complexes (Paleozoic complex on the southern edge of the Fergana basin; and the Permo-Triassic complex on the southeastern edge of the Uinta basin). The distribution of bitumen accumulations in the orogenic complexes of these basins is controlled by fault zones within the oil and gas structures as, for instance, in the South Fergana fold zone and zones where oil-and-gas complexes pinch out. An example of this is the Green River Formation, on the edge of the Uinta-Piceance Basin.

In composition, the bitumens of these basins are exceedingly diverse. In addition to asphaltic varieties, ozokerite is widespread, forming the economic accumulations in the West Turkmenian and Fergana Basins.

1.4 PRINCIPAL BITUMEN ZONES AND RESOURCES IN THE FORMER SOVIET UNION

On the basis of models of bitumen formation that have been developed and analysis of the conditions of distribution of accumulations of natural bitumens in the oil and gas basins of the world, Goldberg (1981) predicted zones of bitumen accumulation in the former Soviet Union and made the first preliminary estimate of the natural bitumen resources. The most promising zones, containing substantial concentrations of natural bitumens, were:

a. In East Siberia, the outer edge of the Verkhoyansk, Lena-Anabar, and possibly the Yenisey-Khatanga marginal depressions adjacent to eroded uplifts of the craton. On the basis of a combination of indices, these zones are favorable for the formation of large bitumen accumulations, chiefly of maltha-asphalts. They are controlled by zones in which oil and gas complexes pinch out or change lithologically: (1) the Permian, on the monoclinal slopes of the Olenek Arch, where the very large Olenek deposit, with resources of 1.3 billion tons, has already been found; and (2) the Lower Jurassic, on the southeast slope, and probably the Permo-Triassic, on the east slope, of the Muna Arch.

b. In the Volga-Urals Province, the junction zones between large intra-cratonic arches (south and north domes of the Tatar Arch, Tokmovo and Zhiguli-Pugachev Arches) and basins (Melekess,

Stavropol'), which constitute a single district of Permian bitumen accumulation, including the proven part in Tatary. This district is of the intra-cratonic type and contains numerous local accumulations of bitumen and highly viscous oils controlled by local structures and lenticular bodies, particularly sand bars. A controlling factor in the distribution of pools in the Ufan and Kazanian deposits, which contain the main natural bitumen resources of the district, is the presence of deep erosional cuts related to the development of pre-Neogene and Recent river valleys. These two deposits resulted from vertical migration of petroleum, probably from the Carboniferous deposits, along fracture zones reflected in the present drainage network, and subsequent transformation of the petroleum during Neogene-Quaternary time by fresh water infiltrating along these zones.

c. In the Timan-Pechora Province, zones of uplift occur, with intensive growth in several stages: Late Frasnian-Tournaisian, Viséan-Artinskian, Kungurian-late Permian, and Triassic-Early Jurassic,accompanied by deep erosion of the crests of folds, which promoted the destruction of oil pools. The most favorable places for finding large stratiform deposits of bitumen, both asphalt asphaltite, are: (1) the Varandey-Adz'va zone ("Zinchenko" paleo-arch), in Carboniferous-lower Permian deposits beneath the pre-Triassic pre-Middle Jurassic erosion surface; (2) the Omra-Soyva paleo-uplift, in the deposits of the zone below the pre-Viséan hiatus; and (3) the Central Pechora paleo-uplift, in Carboniferous deposits beneath the pre-Kungurian erosion surface. The prospects for finding considerable reserves of highly viscous oils, the malthas, are related to zones underlain by thick sandstone sequences, probably deltaic, in the northeastern part of the province and, in particular, in the north block of the Sorokin rise.

d. In the Volga-Emba district, zones of active Cenozoic and Recent uplift with amplitudes of 200–350 m are found between the South Emba and Kenkiyak oil regions. Middle Jurassic-Lower Cretaceous oil fields have been brought to or near the surface above salt-dome structures and transformed into kir accumulations.

e. In the Mangyshlak oil and gas district may be seen contrasting structures in the Beke-Bashkuduk and Tyub-Karagan rises, uplifted with amplitudes of more than 200–250 m in pre-Neogene and Neogene-Quaternary time.

The prospects for increasing the reserves of natural bitumen in other parts of the country, including the Apsheron-Kobystan, Kura, West Turkmenian, and Fergana Basins and the Cis-Carpathian and West Kuban Depressions, were examined.

Prospecting and exploration in the last 10 years has made it possible to give a fairly sound estimate of the natural bitumen resources in the Volga-Urals Province and in the Ural-Emba and Mangyshlak oil and gas districts. For the other oil and gas regions of the former Soviet Union (East Siberia, Central Asia, and northern European), determination of the amount of predicted resources remains at the level of an educated guess.

On the whole, the estimated reserves of natural bitumens for the former Soviet Union and Azerbaijan currently are estimated at a level of 17 billion tons, including 3.3 billion tons at concentrations of more than 5 wt% (Table 1.7). The value 3.3 billion tons of predicted reserves can be considered the basis for future planning of prospecting, exploration, and test-commercial work on natural bitumens.

The details of the composition and properties of the bitumens of the various regions, and the presence or absence of useful by-product components in them, particularly metals, require differing

TABLE 1.7
Natural bitumen resources of the former Soviet Union and Azerbaijan
[Source: VNIGRI, IGIRGI, and MNTK "Nefteotdacha" and "Taneft"]

Province (district)	Predicted resources (million tons) Category of resources			Resource distribution by bitumen saturation (million tons)		Distribution of resources by depth (million tons)		Main classes of bitumens
	$D_1 + D_2$	D_1	D_2	< 5 wt%	≥ 5 wt%	0–50 m	50–500 m	
Volga-Urals	6270	4030	2240	4285	1935	480	5790	Extra-heavy oils, maltha, asphalt, asphaltite
Timan-Pechora	477	407	70	477	–	127	350	Asphalt, maltha, asphaltite
North Caspian	890	765	125	–	890	75	815	Maltha, extra-heavy oil
North Caucasus-Mangyshlak	390	230	160	10	380	45	345	Maltha, extra-heavy oil
South Caspian	110	100	10	70	40	20	90	Maltha, extra-heavy oil, ozokerite
Amu Dar'ya	40	30	10	40	–	–	40	Maltha
Lena-Tungusska	9060	1300	7760	9060	–	4560	4500	Asphalt, maltha, asphaltite
Okhotsk-Sakhalin	2	2	–	–	2	2	–	Maltha
Ferghana	3	2	1	3	–	2	1	Maltha, asphalt, ozokerite
Total FSU and Azerbaijan	17,242	6866	10,376	13,945	3297	5311	11,931	
Total minus East Siberia (Lena-Tungusska OGP)	8182	5566	2616	4885	3287	751	7431	

approaches to the evaluation of the resources and choices for the direction of integrated use of bitumen raw material.

Volga-Urals Province

In this province, 1,985 million tons, with a saturation of ≥5 wt%, are promising, out of total bitumen and extra-heavy oil resources of 6270 million tons. The distribution of these resources, estimated by I.M. Akishev and G.A. Petrov, is as follows (million tons):

Ufimian stage (South Tatar arch)	780
Ufimian stage (west flank of South Tatar arch)	625
Sakmarian stage (west flank of South Tatar arch)	104
Kazanian stage (Melekess basin and west flank of South Tatar arch)	476
Total	1,985

The Permian natural bitumens contain substantial resources of vanadium, nickel, and other metals (see Chapter 6), with maximum vanadium concentrations in the bitumens of the Kazanian stage.

At present, as a result of the prospecting and exploration that has been done, 742 million tons of the estimated potential bitumen resources are assigned to reserves category C_3, 449 million tons to category C_2, and 309 million tons to category C_1. Altogether, 75 deposits of natural bitumen, 24 of which have been proven, have been found in Tatary. These bitumen deposits are worked by wet combustion and cyclic steam injection. On a test area of the Mordovo-Karmal'sk deposit, flows of 0.05 to 15 m^3 per day of extra-heavy oil were obtained as a result of the application of thermal enhanced recovery.

West Kazakhstan

In West Kazakhstan (Mangyshlak Peninsula of the North Caspian Province), bitumen resources of 1,280 million tons are concentrated; most of these are assigned to the promising category. Because of their unique properties, the bitumens can be used to obtain the components of motor fuels and oils with low freezing points, high-octane gasoline, valuable chemical products based on hetero-organic compounds (sulfones, sulfoxides, *etc.*), and low-sulfur coke. In addition, the bitumens have already found application in road construction.

At present, 45 structures, 41 in the North Caspian Basin and four on the Mangyshlak Peninsula, have been prospected and, to varying degrees, proven. During 198586, the large Mortuk and two medium-sized deposits, the Tyubedzhik and Akzhar, were discovered. In the Mortuk deposit the bitumen reserves (maltha) are 62.3 million tons, 54.5 million tons of which are concentrated in Lower Cretaceous sandy horizons at depths of 6 to 52 km. In the Akzhar deposit, the economic reserves of bitumen are estimated at 17.7 million tons, with an average bitumen content of 9 wt%.

Exploration for kir rocks for road construction is being conducted extensively. According to predictive estimates, the total resources of kir rocks in West Kazakhstan, to a depth of 50 m, are 120 million tons. In a number of deposits (Altay, Munayly-Mola, Iman-Kara, *etc.*) the kir rocks are mined by the open-pit method. Kirs are used to obtain asphalt-concrete mixtures. On the whole, the bitumens

of West Kazakhstan have very low concentrations of rare and disseminated elements and, particularly for road construction, need no demetallization of the raw material in order to eliminate the harmful effect of toxic compounds.

Timan-Pechora

In the Timan-Pechora Province the predicted bitumen resources are estimated at 477 million tons, but most of the accumulations are relatively poorly saturated with bitumens (25 wt%), the bitumens are altered asphalt and asphaltite, with about half the resources hosted in carbonate rocks. A plus value is the shallow depth of occurrence (up to 50 m) of most of the bitumen accumulations, including the largest (Izhemsk, Voyskoye, Tal'tinskoye, Kozhva-Kamenskoye), which permits consideration of the natural bitumen resources for local road construction and building, as well as for the paint and varnish, chemical, and other industries. In addition, a number of bitumen deposits contain economic concentrations of vanadium, nickel and other elements (see Chapter 6).

South Caspian Province

In the South Caspian Province (Azerbaijan and Turkmenia), the predicted resources of natural bitumens are estimated to be 110 million tons, of which 36 percent are promising. The main bitumen resources are concentrated in the Apsheron-Kobystan region, where many bitumen deposits were worked earlier to obtain asphaltite mastic and, on a test scale at the Kirmaku deposit, to obtain liquid fuel. At present, the highly resinous crude oils, or malthas, in shallow layers of the productive sequence and also in the Chokrak, may be of interest for commercial development at Kirmaku, Ayrantekyan, Umbaki, and other deposits. The surface kirs at Kirkishlak, Akhtarma-Pashaly, and Atashka-Shubany may also be of commercial interest. In addition, fairly large outcrops of kirized rocks in the Balkhash area on the Cheleken Peninsula, with saturations $\geq$15 wt%, may be used as raw material for road construction.

East Siberia

In East Siberia, in the Lena-Tungusska and Lena-Anabar Provinces, the predicted resources of natural bitumens, according to educated guesses, are 9,065 million tons. No prospecting or exploration for bitumens has been done, except for earlier (1966–68) evaluation of the Olenek deposit. Extensive zones of bitumen-saturated rocks found at the surface in the clastic-carbonate Vendian-Cambrian complex of the East Anabar and Siligir-Markha deposits, probably contain large asphalt and asphaltite bitumen resources, but they have hardly been studied. Negative points in developing the bitumens of East Siberia are their location in virtually uninhabited regions and detailed data on the accumulations which, despite their large resources, amounting to more than half the total bitumen resources of the former Soviet Union, have low bitumen concentrations (2 wt%). Bitumen resources with a concentration of 2–5 wt% constitute no more than 15–18 percent of the total resources, and most of them are in the Olenek deposit, where the average bitumen concentration is only 2.9 wt%. Except for the Olenek deposit, the bitumens of East Siberia, on the whole, have a low concentration of vanadium, nickel and other metals.

Thus, the investigations that have been made in the former Soviet Union indicate that in the near future most geological exploration and test-commercial work aimed at developing the natural bitumen resources should be concentrated in two regions, Volga-Urals and West Kazakhstan. The key problems in developing bitumen deposits are the solution of technological problems involved in their production and in the integrated refining required to obtain not only hydrocarbons, but also other valuable components in them, particularly metals. This primarily concerns the natural bitumens of the Volga-Urals Province, which could be an additional source of vanadium and other rare elements.

2

RARE AND DISSEMINATED ELEMENTS IN OIL AND BITUMEN

More than 60 rare and disseminated elements have been found in petroleum and natural bitumens. In addition to the mainly lithophilic major elements (Al, Mg, Ca, Na, K), other elements disseminated in the earth's crust are V, Ni, Zn, Mo, Cr, Cu, Co, Rb,Se, As, Ga, Ge, Hg, Cd, Sb, Bi, Re, Ce, and Ag (Figures 2.1 and 2.2). It can be assumed that as highly sensitive methods of analysis are developed, practically all the elements of the Periodic Table that are stable over geological time will be found in petroleum in subclarke and ultra-subclarke amounts. In addition, the combination of rare and disseminated elements found in above-clarke concentrations is fairly limited, consisting of V, Ni, Mo, Re, Ag, Au, As, Hg, Sb, Se, and U and, less often, Ge and Sc. In most cases, relatively high concentrations of these elements are typical only of heavy oils and bitumens. Elements that are economically valuable at present include V, Ni, and Hg in petroleum and V, Ni, and U in bitumens. Numerous reports by our own and foreign authors have been devoted to rare and disseminated element composition of petroleum and bitumens and their components (Vinogradov, 1936; Gulyayeva, Itkina, and Romm, 1941; Ketchenkov, 1959; Zul'fugarly, 1960; Hyden, 1961; Shah, Filby, and Haller, 1970; Filby, 1975; Yen, 1975; Valkovic, 1978; Antipenko, Melkov, and Titov, 1979; Kam'yanov, Aksenov, and Titov, 1983; Nadirov, Korova, Kam'yanov *et al.*, 1984; Chakhmakhchev, Punanova, and Lositskaya, 1984; Moore and Ramamoorthy, 1987; and others).

These investigations of the rare and disseminated elements in petroleum and bitumens were of different kinds, encompassing a broad range of problems:

1. refining crude oil and assessing the role, often negative, of rare and disseminated elements in technological processes in order to choose the optimal schemes of refining and improving the quality of petroleum products;
2. protecting the environment and, in particular, identifying toxic compounds in fuel oils which, when burned at power stations, eject a substantial amount of harmful substances into the atmosphere;
3. ascertaining commercial by-products (V, Ni, *etc.*) in order to enhance the efficiency and combination of the refining of petroleum and bitumen raw material;
4. relating geology and geochemistry to the origin of petroleum, analysis of petroleum-producing formations, migration of petroleum, formation of pools, and transformation of petroleum.

Despite the different approaches and different analytical methods used to determine the metals, fairly unambiguous results were obtained on the general patterns of distribution of rare and disseminated elements in crude oil and bitumen and on the relationship of certain elements, or groups of elements, to certain petroleum fractions and compounds.

According to Kam'yanova, Aksenov, and Titov (1983), all rare and disseminated elements in petroleum compounds except soluble salts and inorganic colloids fall into the following main groups:

1. organo-elemental compounds containing a carbon-element bond;
2. salts of metals;
3. chelates, the intramolecular metal complexes (metalloporphyrins);
4. complexes of several of the same or of mixed ligands;
5. complexes with heteroatoms or π-system polyaromatic asphaltene structures.

It has been proposed (Yen, 1975) that metals such as Pb, Hg, As, Sn, Ge, and Tl can also form organoelement compounds. Pb forms alkyl and aryl compounds of the tetraethyl lead type, which are

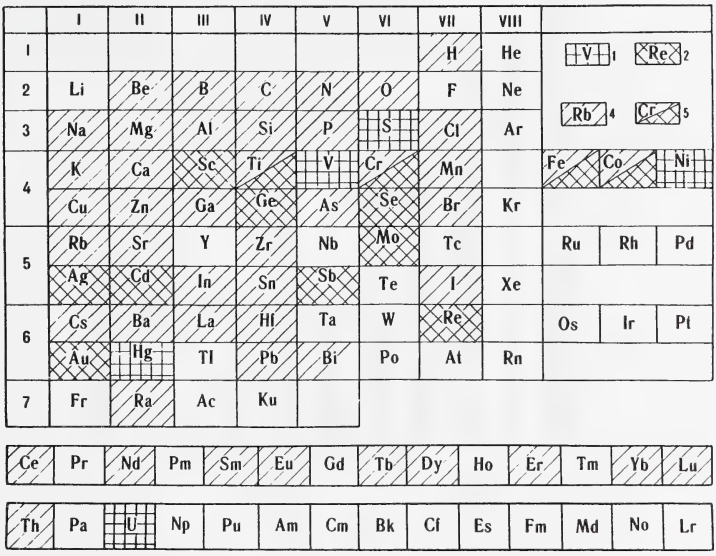

I II III IV V VI VII VIII
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni
Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd
Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt
Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac Ku
V 1 Re 2
Rb 4 Cr 5
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

FIGURE 2.1

Chemical elements in petroleum and natural bitumen

1 – By-product elements of economic value

2 – Potentially valuable elements

4 – Other chemical elements found in petroleum and bitumen

5 – Possible additional elements for use in pyrometallurgy

3 – Recorded levels of elemental concentrations (%)		
Element	In petroleum	In bitumen
S	1.5 – 4.5	3.0 – 7.5
Sc		$5.0 \cdot 10^{-4} - 1.0 \cdot 10^{-2}$
V	$0.2 \cdot 10^{-1} - 1.41 \cdot 10^{-1}$	$0.4 \cdot 10^{-1} - 6.2$
Ni	$0.1 \cdot 10^{-1} - 0.2 \cdot 10^{-1}$	$0.5 \cdot 10^{-1} - 1.2 \cdot 10^{-1}$
Ge		$0.1 \cdot 10^{-1} - 0.15 \cdot 10^{-1}$
Se		0.05 – 0.2
Mo	$5.0 \cdot 10^{-4} - 15 \cdot 10^{-4}$	$2.0 \cdot 10^{-3} - 1.0$
Ag		$1.5 \cdot 10^{-4} - 5.0 \cdot 10^{-4}$
Cd		$1.5 \cdot 10^{-3} - 2.7 \cdot 10^{-3}$
Sb	$0.5 \cdot 10^{-3} - 4.0 \cdot 10^{-3}$	
Re	$0.1 \cdot 10^{-4} - 0.21 \cdot 10^{-4}$	$0.8 \cdot 10^{-4} - 1.01 \cdot 10^{-4}$
Hg	$0.1 \cdot 10^{-3} - 2.9 \cdot 10^{-3}$	

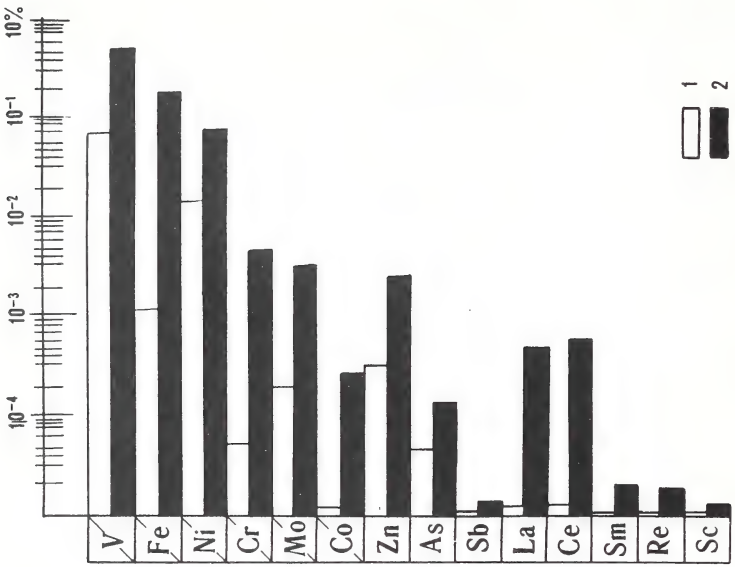


FIGURE 2.2

An example of the correlation of ore elements in heavy crude oil and in petroleum coke

1 – heavy crude oil

2 – petroleum coke

used extensively as antiknock additives to gasoline. Hg, in addition to being present in complexes with various organic ligands (especially sulfur-containing ligands), can form alkyl-mercury or aryl-mercury compounds. Arsenic is firmly bound to S and C in organic compounds of the As^{3+}-C and As^{5+}-C types.

Non-porphyrin V and Ni, as well as Mo, Zn, Cr, and other heavy metals are probably present in petroleum in the form of salts.

Among the metalloporphyrin complexes in petroleum and bitumens, only V and Ni have been reliably established, although other elements (Zn, Fe, Cu) are assumed to be present. There are two main points of view concerning the nature of petroleum porphyrins. The dominant hypothesis, which has been experimentally confirmed in recent years (Serebrennikova, 1988), recognizes the genetic unity of petroleum porphyrins and the pigments of biological systems; chlorophyll, which plays an essential part in the life activity of the micro and macroflora of offshore regions of the seas, is believed to be the precursor of most petroleum porphyrins. According to the "bacterial porphyrin" hypothesis (Radchenko, 1974; and others), vanadyl porphyrins are formed in petroleum as a result of biochemical oxidation of petroleum in contact with water, with the active participation of sulfate-reducing bacteria. The petroleum is enriched in sulfur and asphalt-resin components. Hodgson and Peak (1961) believe that such a process can occur under conditions of sedimentogenesis in the case of hydrogen sulfide contamination, when V^{5+} is reduced and (VO), capable of complexing with porphyrins, is formed. The amount of vanadium in porphyrins ranges from 20 to 40 percent in various petroleums, averaging about

25 percent on the basis of a large number of determinations. The concentration of vanadium porphyrins in some heavy, high-sulfur oils reaches 1500–3000 g/t and in asphaltites, as much as 6000 g/t.

Most rare and disseminated elements are bound to polycyclic structures of petroleum and bitumens. According to Filby (1975), the concentration of most rare and disseminated elements increases with molecular weight. The only exception is part of the V, Ni, and Sb; the first two are concentrated in the fractions with a molecular weight close to the weight of the corresponding porphyrin complexes, while Sb predominates in the low molecular weight part. Asphaltenes, which contain the maximum concentration of most heavy metals per unit of matter, also have a relatively high content of heteroatoms (N, O, S) which enter into all groupings found in petroleum. Experiments on the extraction of nonferrous and precious metals (Gerasimova, Nesterenko, Sagachenko *et al.*, 1979) from dilute aqueous solutions, using petroleum asphaltenes indicate the high capacity of asphaltene molecules for bonding of metals.

For the first time, the ash of petroleum and bitumens from a number of fields in the Volga-Urals, Timan-Pechora and Lena-Vilyuy oil and gas provinces was studied using X-ray phase analysis (Goldberg, Kaplan, and Ponomarev, 1986) (Table 2.1). The diffractograms of the ash indicate that it is a multiphase crystal system, whose identification is complicated by the frequent and sometimes complete superposition of reflections of individual phases. Table 2.1 includes only reliable phases, in which the main analytical reflections on the diffractograms are the most intensive and mostly not superposed.

On the basis of Z.G. Kaplan's interpretation of the diffractograms, three main groups are distinguished, containing: (1) salts of inorganic acids, mainly sulfates, carbonates, and chlorides; (2) sulfides; and (3) metal oxides. The composition of the salts is close to that of the formation waters. This is especially obvious in the ash of petroleum from the Radayevskoye and Sernovodskoye Fields, which contain mainly chlorides, carbonates, and sulfides of Na, Ca, Mg, and Fe. The chemical composition of the phases containing rare and disseminated elements consists mainly of metal sulfides and oxides, and, much more rarely, salts. For instance, Ni, Zn, Cu, and Pb are often found in the form of salts; however, Ni and Zn sometimes are contained in sulfates, and Pb in carbonates. Metals such as V, Ti, and Mn usually are present in the ash in the form of oxides (V_2O_3, V_2O_5, TiO_2, and MnO_2). Zn and Pb also occur in the form of oxides, but rarely. Sulfides and oxides occur both as simple forms of the NiS, ZnS, and PbS types, and as complex forms of the Cu_2S $2FeS_2$ or Cu_2S Fe_4S_5 (cubanite) types. In the oxides, the valency of some heavy metals varies from the lowest form (Cu_2O) to the highest (V_2O_5).

It is noteworthy that in relatively light oils (Khar'yaga Field), it is mostly the elements that are concentrated not only in the residual but also in the high-boiling fractions in petroleum (Pb, Cu, Zn) that are present in the crystalline phase.

As a result of the X-ray investigations, it also was established that the crystalline phases of the ash of Ural-Volga petroleum and bitumens are identical or close in metal content. This may indicate that the rare and disseminated elements in the petroleum and bitumens have a common source.

When petroleum is ashed, a loss of rare and disseminated elements capable of forming volatile compounds with low molecular weight components of petroleum, or with the products of the decomposition of the petroleum, cannot be taken into account. Moreover, under the influence of carbon dioxide gas, some compounds may decompose during the ashing of petroleum. In particular, the latter can explain the absence of vanadium sulfides in the ash and the presence of titanium only in dioxide form, that is, as rutile (TiO_2) and not as the sulfide (TiS_2).

TABLE 2.1
Identification of the crystalline phase of the ash from petroleum and natural bitumen

Field	Depth (m)	Producing horizon	Original substance	Chemical composition of crystalline phases
Gorskoye	289 – 302	P_2KZ_1	Maltha Residue at 500°C	V_2O_5; TiO_2; Fe_2O_3; $CaSO_4$; Cu_2S Fe_4 S_5 V_2O_3; TiO_2; Fe_2O_3; $CaCO_3$; $CaSO_4$; Na_2SO_4; $ZnMn_2O_4$
North Katerga	281 – 284	P_2KZ_1	Highly resinous petroleum	V_2O_3; FeO; $CaSO_4$; $CaMg(CO_3)_2$; $CaCO_3$; $Cu_2S{\cdot}Fe_4S_5$
Ivankino-Malaya Sul'cha	1190 – 1203	C_1V	Heavy oil	V_2O_3; TiO_2; FeO; $CaMg(CO_3)_2$; $CaCO_3$; Mn(OH)O; SiO_2
Nurlaty	1257 – 1265	C_1V^{bb}	Heavy oil	V_2O_5; FeO; $CaCO_3$; $CaMg(CO_3)_2$; SiO_2
Sadki mine	137.5	P_2t	Asphaltite	V_2O_3; NiS; $CaCO_3$; Na_2SO_4; FeS_2; SiO_2
Radayevskoye	1385	C_1	Heavy oil	V_2O_3; NiS; $NiSO_4{\cdot}7H_2O$; $CaSO_4{\cdot}H_2O$; $CaCO_3$: Na_2SO_4; $CaMg(CO_3)_2$
Radayevskoye	2130	D_2	Heavy oil	V_2O_3; $V_2O_4{\cdot}3SO_3{\cdot}16H_2O$; β-NiS $SrSO_4$; $CuS{\cdot}2FeS$; MnS; $SrCO_3$; $NiSO_4{\cdot}7H_2O$; $CaSO_4{\cdot}2H_2O$; CaS; $2Na_2SO_4{\cdot}Na_2CO_3$ $CaCO_3$; $CaSO_4$; NaC1; $CaMg(CO_3)_2{\cdot}CaS$
Sernovdskoye	914 – 930	C_2	Heavy oil	V_2O_3; NiS; $V_2O_4{\cdot}3SO_3{\cdot}16H_2O$; $NiSO_4{\cdot}7H_2O$; Cu_2O; $SrSO_4$; Na_2B_4O7; Na_2SO_4; $CaSO_4$; CaS; NaC1; $2Na_2SO_4{\cdot}Na_2CO_3$

Table 2.1 cont'd ...

Field	Depth (M)	Producing horizon	Original substance	Chemical composition of crystalline phases
North Sorokinskoye	1105 – 1121	T_1	Heavy oil	V_2O_3; NiS, TiO_2; $CaSO_4$; SiO_2; MnS_2
Khar'yaga			Light oil	β-NiS; $PbCO_3$; β-Cu_2S·PbS; $SrCO_3$; $BaSO_4$; CuS·2FeS; PbO_2; $NiSO_4·7H_2O$; ZnS; $ZnMn_2O_4$; MnO_2; Na_2SO_4; $Fe_2O_3·H_2O$; CaS; $CaMg(CO_3)_2$; SiO_2; $CaSO_4$; $CaCO_3$
Middle Tyung	2990 – 2998	PZ	Oil fringe	CuS; TiO_2; NiS; $NiSO_4·7H_2O$; $ZnMn_2O_4$; MnO_2; $Ni_2Pb_2S_2$; $Fe_2O_3·Na_2SO_4$; $FeSO_4·7H_2O$; CaS; $BaSO_4$; $CaCO_3$; SiO_2 $CaMg(CO_3)_2$; $CaSO_4$; SiO_2

Analysis of the rare and disseminated element distribution in the petroleum fractions is exceptionally important for understanding the chemical nature of metallic compounds of petroleum and bitumens. However, a small amount of geochemical work has been done in this direction and it pertains to a limited range of elements.

In the mode of distribution of elements in petroleum and bitumens, two main groups of elements can be distinguished, on the basis of available data: (1) Mo, V, Ni, Sb, Cr, Co, Au, Ag, Ga, and U, bound to the residual fractions of petroleum, where they are concentrated in the resin and asphaltene components, or chiefly, in the case of Mo and Sb, only to the asphaltenes; and (2) Hg, Pb, As, Cu, Zn, Se, Sn, Fe, and Sc, present in all petroleum fractions, including gasoline in the case of As and Hg. The maximum concentration of group (2) is observed in the residue.

The percentage of each element in certain fractions of various petroleums and bitumens is different and may vary within fairly wide limits. This depends on the genetic nature of the elements in the petroleum, and the composition (heteroatomic or functional), conditions of formation, and extent of alteration of the petroleum.

According to Filby (1975), the concentration of elements in the fractions of California oils takes the following form: in oils, 2.0 to 4.6 percent of the Ni, Co, Fe, Hg, Zn, and Sb; in the resins, 7.2 percent of the Sb, 20.3 percent of the As, 35–38 percent of the Zn, Cr, Fe, and Co, and 54–60 percent of the Ni and Hg; and in the asphaltenes, 21 percent of the As, 37–59 percent of the Ni, Co, Hg, and Zn, and 90 percent of the Sb.

In the oil sands of Alberta (Athabasca, Cold Lake, and Peace River deposits), the asphaltene fraction of the bitumens contains 48–55 percent of the Sc and Se, 63–67 percent of the As, Co, Fe and Hg, 72–77 percent of the Ni, V, and Cr, and 86–96 percent of the Ga, Sb, and Mo. The resins contain 0.6–2.5 percent of the Mo and Fe, 10–20 percent of the Ni and Cr, and up to 30 percent of the V. The highest percentage content of Se and Sc is found in the oil fractions.

In the crude oil of West Siberia (the Russkoye, Sovetskoye, Samotlor, and Salym deposits), not more than 42–44 percent of the V, Ni, and Co is bound to asphaltenes (Aleshin, Kam'yanov, Filimonova, and Gorbunova, 1986). In only two out of thirteen carefully analyzed samples was more than half of the total amount of Zn, Sc, Cr, Sb, and Se contained in the asphaltene fraction; much more often, 60–90 percent of the elements fell in the resin part of the crude. Such partitioning of metals (V, Ni, *etc.*) between resins and asphaltenes is typical of low-asphaltene petroleum, in which the content of asphaltenes is much lower than that of resins. This is because most heavy metals accumulate in the resins when petroleum is fractionated, although their unit concentration in the asphaltenes is higher. For high-asphaltene petroleum and bitumen, the opposite relationships are observed in the partitioning of absolute contents of V, Ni, Cr, and other elements between the asphaltenes and resins. This is seen in the heavy oils and bitumens of the Volga-Urals area and Tadzhikistan.

This conclusion is graphically illustrated by the data of an investigation of the residues of heavy oil from the Arlan field in Bashkiria and a commercial mixture of West Siberian petroleum. In the residues above 540°C of the Arlan crude, most of the vanadium (71.6 percent) and nickel (60.5 percent) is contained in the asphaltenes; in the residues of the West Siberian crude, most of the vanadium (56.4 percent) and nickel (34.4 percent) is in resins II, although the absolute concentrations of metals in the asphaltenes are much higher (Table 2.2).

In the hydrocarbon fractions of distillates from residues of both the West Siberian and Arlan crude oils, the content of V and Ni is extremely low, especially in the paraffinic-naphthenic and light aromatic hydrocarbons (Table 2.2).

TABLE 2.2
Distribution of vanadium and nickel on the basis of chromatographic fractions of petroleum residues

Petroleum products and their characteristics	Group chemical composition of petroleum residues						
	Paraffinic-naphthenic	Light aromatic	Medium aromatic	Heavy aromatic	Resins I	Resins II	Asphaltenes
Residue above 540°C of industrial-grade mixture in W. Siberian petroleums							
Yield of residue (wt%)	7.20	7.70	7.80	31.80	18.80	20.40	6.30
Content of V (10^{-4} wt%)	0.10	6.50	13.00	26.00	110.00	470.00	692.00
% of total in residue	0.04	0.29	0.60	4.86	12.16	56.41	25.60
Content of Ni (10^{-4} wt%)	0.10	0.50	0.50	13.00	110.00	120.00	343.00
% of total in residue	0.01	0.05	0.06	5.82	29.13	34.48	30.00
Residue above 540°C in Arlan petroleum							
Yield of residue (wt%)	4.100	5.90	5.800	26.90	19.50	19.80	18.00
Content of V (10^{-4} wt%)	0.120	4.82	9.740	14.11	352.00	411.00	2174.00
% of total in residue	0.001	0.05	0.100	0.70	12.58	14.91	71.68
Content of Ni (10^{-4} wt%)	0.110	0.44	0.220	41.45	335.90	112.00	840.30
% of total in residue	0.002	0.01	0.005	4.46	26.20	8.87	60.50

As the depth from which the distillates from the petroleum residues were collected increases, an increase in the content of heavy metals (V, Ni, Co, Cr, Mo) is observed everywhere, which leads to their multiple concentration in the residues and resins compared to the crude oil. For instance, in the refining of Venezuelan petroleum, which contains 136 g/t of vanadium and 18 g/t of nickel, their concentrations in the residue reach 475 g/t and 42 g/t, respectively (Bergerioux, Galinier, and Vikovsky, 1979). Likewise, with increasing temperature of the fractions of the Arlan and West Siberian crude oils, the concentrations of V and Ni increase abruptly (Table 2.3). Such analytical data

TABLE 2.3
Distribution of vanadium and nickel in petroleum residues

Indicator	Residues of industrial-grade mixture of West Siberian oils, boiling above: (°C)			Residues of Arlan oil, boiling above: (°C)		
	480	540	590	400	540	580
Yield (wt%)	24.500	16.70	12.60	47.00	26.50	21.00
Density (kg/m^3)	986.300	1014.00	1029.00	1012.00	1051.00	1062.00
Conradson carbon	12.500	18.40	23.10	17.20	27.00	28.00
Ash (wt%)	0.091	0.05	0.12	0.15	0.15	0.17
Metal content (wt%·10^{-4})						
Vanadium	120.000	170.00	240.00	310.00	546.00	650.00
Nickel	46.000	71.00	84.00	150.00	250.00	320.00

on the concentration of metals in different products of petroleum distillation can be found in a large number of publications. These investigations have been especially extensive in the field of refining of petroleum residues by catalytic processes, because of the contamination of the catalysts by metals (V and Ni), which are precipitated on the active surfaces of the catalysts.

On the basis of analysis of trends of distribution of various elements during fractionation of petroleum and bitumens, geochemical indicators of the process of generation and migration of petroleum and the catagenesis and supergenesis of petroleum have been worked out (Chakhmakhchev, Punanova, and Lositskaya, 1984).

However, most investigations of rare and disseminated elements in petroleum and bitumens have been of an empirical nature, without analysis of the chemical structure of the metal compounds. The only exception is the porphyrin compounds in crude oil and bitumens, from which individual compounds have been analytically separated, and the values of their retention and spectral characteristics have been determined. The need for detailed study of the chemical structure of other metal compounds is obvious. Work in the field of the chemistry of metal compounds in petroleum could open up new paths to the solution of practical problems in the extraction of rare elements, the refining of crude oil, and the development of new directions in rare and disseminated element geochemistry.

3

METALLOGENIC SPECIALIZATION OF OIL AND GAS PROVINCES AND THE ORIGIN OF ORE CONCENTRATIONS IN HEAVY OIL AND BITUMEN

3.1 PRINCIPLES OF REGIONALIZATION

The ascertainment of regional trends governing the accumulation of rare and disseminated elements in petroleum and natural bitumen was based on our naphthometallogenic regionalization of oil and gas districts (Figure 3.1). This reflects the distribution of rare and disseminated elements in petroleum and bitumens on the basis of both their absolute concentrations and the associations of elements characterized by maximum values of the concentration coefficients (C_c), the ratio of the content of an element in petroleum or bitumen to its clarke for sedimentary rocks (Vinogradov, 1962).

In calculating the order of concentration of rare elements in petroleum and bitumens, we used a large amount of analytical data obtained by the emission spectral analysis method in the VNIGRI laboratory in St. Petersburg. In studying the quantitative distribution of rare elements at both clarke and sub-clarke levels, we used the results of neutron activation analysis of suites of crude oils and bitumens that I collected especially. The samples enriched in rare elements, particularly in V and Ni, were investigated in the VNIGRI by X-ray fluorescence analysis, which is fast, highly sensitive, and precise.

In addition, available data on the rare and disseminated element composition of petroleum and natural bitumens, published in our own and in the foreign literature, were called upon.

The order of concentration of rare and disseminated elements in crude oils and bitumens was calculated for virtually all the oil and gas basins of the former Soviet Union (Timan-Pechora, Volga-Urals, North Caspian, South Caspian, West Siberian, East Siberian, Lena-Vilyuy, Fergana, Surkhan-Vakhsh, and others), as well as for many basins in other countries (Canada, United States, Venezuela, Egypt, Saudi Arabia, Libya, Italy, Germany, Albania, and others.

Analysis of the distribution of rare and disseminated elements shows that, for the most part in producing complexes in individual oil and gas basins, a relatively stable order of concentration of elements is observed, despite wide fluctuations in the content of each element. This enables us, on the basis of determination of associations of elements or individual elements that are dominant in petroleum and bitumens, to ascertain the metallogenic specialization of the oil and gas provinces and to classify them. We distinguished the types of naphthometallogenic provinces on the basis of rare and disseminated elements whose absolute concentrations are at least 50 percent of the total metal content of the petroleum and bitumens; the subtypes were distinguished on the basis of rare and disseminated element associations that have stable maximum values of the concentration coefficients. Despite the seeming diversity of rare and disseminated element compositions of petroleum and bitumens, this approach to their classification made it possible to distinguish, on the basis of a relatively limited combination of dominant rare elements, just three main types of naphthometallogenic provinces: (1) vanadium and nickel-vanadium; (2) nickel and vanadium-nickel; and (3) zinc (Table 3.1) (Goldberg, 1989a,b, 1990, 1991). Besides having different associations of elements, each of these types has different total concentrations of rare and disseminated elements in petroleum and bitumens, including extreme values in the concentration of the dominant elements. Therefore, this classification provides the material needed to substantiate the metallogenic regionalization of oil and gas basins used as the basis for regional prediction of their metal potential.

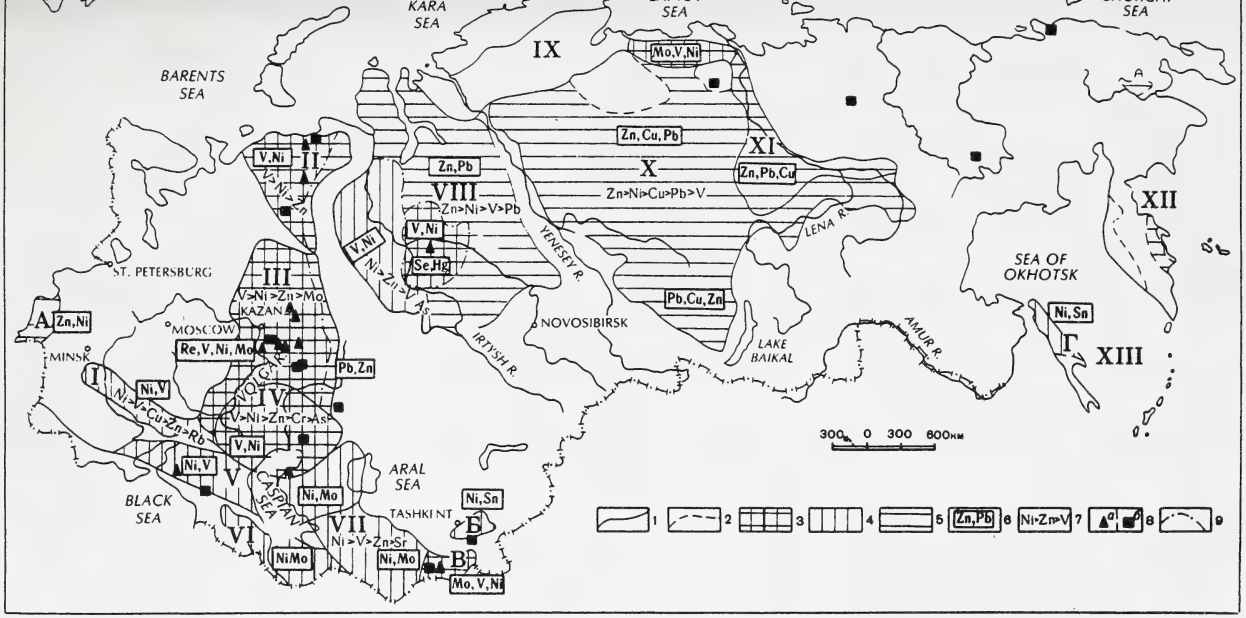


FIGURE 3.1

Naphthometallogenic map of the former Soviet Union [Compiler: I.S. Goldberg]

1 – Boundaries of oil and gas provinces and areas
2 – Boundaries of prospective areas
3 – Naphthometallogenic provinces and areas of the nickel-vanadium (Ni-V) type
4 – Naphthometallogenic provinces and areas of the nickel (Ni) type
5 – Naphthometallogenic provinces and areas of the zinc (Zn) type
6 – Principal stable associations of elements in petroleum and bitumen
7 – Decreasing order of abundance of elements in stable associations
8 – Principal deposits of metalliferous heavy oil (a) and bitumen (b)
9 – Boundaries of naphthometallogenic areas

Oil and Gas Provinces:

A – Baltic
B – Fergana
Б – Surkan-Vakhsh
Г – Sakhalin
I – Dnepr-Pripya
II – Timan-Pechor
III – Volga-Urals
IV – North Caspian
V – North Caucasus-Mangyshlak
VI – South Caspian
VII – Amu Dar'ya
VIII – West Siberian
IX – Yenisey-Anabar
X – East Siberian
XI – Lena-Vilyuy
XII – Bering Sea
XIII – Okhotsk

TABLE 3.1
Types of napthometallogenic provinces

Type of province	Dominant rare element (absolute concentration)	Metallogenic associations (in order of decreasing C_c)		Main provinces: in parentheses, age of deposits containing metalliferous petroleum and/or bitumens
		Main	Secondary	
Vanadium & nickel-vanadium vanadium	V, V, Ni	Re, V, Ni, Mo	Zn, Pb, Cu, Au, As, Sb, Se, Co, Cr	Volga-Urals (D; C_1; C_2; P), Surkhan-Vakhsh (Ꝑ), Adriatic (N_1)
		Mo, V, Ni	Se, As, Au, Sb, Zn, Co, Cr	Maracaibo (Ꝑ$_3$–N), East Venezuelan (K; Ꝑ–N) West Canadian (K_1), Lena-Anabar (Є$_3$ + P) (J_3; K; N), *etc.*
		V, Ni	Mo, Zn, Sb, Au, Ag, As, Sb, Hg, Cd, Co, Cr	Timan-Pechora (D_3; C–P; T), North Caspian (C; P_1; T; J_2–K_1), Mesopotamian (J_3; K; N), *etc.*
Nickel & vanadium nickel	Ni, V	Se, Ni, V, Mo	Hg, Cd, Zn, Co, Cr, Ga	Los Angeles (N_1–N_2), Great Valley (N_1–N_2), Santa Maria (N_1–N_2)
	Ni	Ni, Mo	Zn, Pb, Cu, V, Au, Ag, As, Cr, Co, Sn	South Caspian (N_1–N_2), Amu Dar'ya (J_2–K), South Mangyshlak (P–T, J_1–J_2)
	Ni, Ni, V	Se, Ni	V, Zn, Cd, Sb, Hg, As, Au, Ag, Cu, Co, Cr	Sahara-Libyan (K_2; Ꝑ$_1$–Ꝑ$_2$), Cisalpine (J_1; Ꝑ$_2$) and others
	Ni	Ni, Zn	Pb, Cu, V, Cr, Sn	North Pri-Ural (J_2; K_1), Baltic (Є$_2$–O_3)
Zinc	Zn	Zn, Pb	Ni, Cu, Co, V, Cr, Mo	Northwest Siberian (K_1–K_2), Uinta-Piceance (C_2–C_3, T)
		Zn, Pb, Cu	Ni, Sn, Mo, Cr, V, Co	Lena-Tungusska (V–Є$_1$), Lena-Vilyuy (P_2; T, J_1–J_3), Cambay (Ꝑ)

3.2 NAPHTHOMETALLOGENIC PROVINCES

Vanadium and Nickel-Vanadium Provinces

Provinces of this type (Figure 3.1) have very high values of total rare element concentrations in petroleum and bitumens. In them, Co, Cr, Mo, Zn, and Sr, along with V and Ni, predominate on the basis of absolute content.

In the former Soviet Union, the Timan-Pechora, Volga-Urals, North Caspian, Middle Ob', Lena-Anabar, and Surkhan-Vakhsh Provinces belong to this type of naphthometallogenic province (Table 3.2). The average concentrations of the main elements in petroleum, V and Ni, range from 0.5 to 130 g/t and 0.2 to 60 g/t, respectively; in heavy, high-sulfur petroleum and maltha, the vanadium concentration reaches 550–1400 g/t, and that of nickel, 120–195 g/t. In solid bitumens, especially asphalt and asphaltite, the vanadium and nickel contents sometimes exceed 4500 and 520 g/t, respectively. The concentration of V in almost all the petroleum and bitumens of these provinces is at least 1.5–2.0 times greater than that of Ni, but in the most vanadium-rich heavy oils and bitumens the V/Ni ratio increases to 4.5–10.0, as in the Melekess Basin, and South Tatar and Orenburg Arches.

For most of the high-vanadium petroleum and bitumens, the association of vanadium and nickel with molybdenum, and also with rhenium, is clearly manifested. This group of organophilic elements has minimum concentration coefficients everywhere. On the basis of the C_c of these elements, two types of relationships are found (Table 3.3):

1. The Re-V-Ni-Mo [V-Ni-Mo] element association is typical of the heavy oils and bitumens of the Volga-Urals and Surkhan-Vakhsh naphthometallogenic provinces and the bitumens (maltha, asphalt, and asphaltite) of the Timan-Pechora and Lena-Anabar naphthometallogenic provinces. Deposits of heavy oil and bitumens with maximum concentrations of the main (V, Ni) and associated (Mo, Re) metals have been found. In particular, the C_c values of vanadium in the heavy oils of the Melekess Basin and South Tatar Arch reach 5.4–8.3; nickel, 1.4–2.0; molybdenum, 1.1–7.5; and of rhenium, 75.0–250.0. A number of fields of heavy oil in these provinces contain substantial resources of vanadium and nickel, which allows them to be considered as "deposits within a deposit".
2. The second type of relationship, V-Ni, is typical of the petroleum of the North Caspian, Middle Ob', and Timan-Pechora Provinces, except for the Varandey-Ad'zva zone (Table 3.3). The C_c of vanadium and nickel in the petroleum of these provinces usually is 0.3–0.5, and only in isolated occurrences of heavy, high-sulfur oil does it reach 1.2–2.0 (V) and 0.7–1.0 (Ni) (in the Karazhanbass, West Tebuk, and Usino-Kushshor Fields).

The natural bitumens (maltha-asphaltite) of the Volga-Urals, North Caspian, and Timan-Pechora provinces and other regions have an Au-As association with above-clarke concentrations of these elements. Maximum C_c values of the elements, established on the basis of single samples, are 12–130 (Au) and 2–10 (As) in the Talora, Upper Orlyanskoye, Kara-Murat, Iman-Kara, and other deposits. In some South Emba petroleum, above-clarke concentrations of Hg and Sb have been found.

For elements such as Zn, Cu, Pb, Cr, Co, La, Sr, Sn, Ga, Hf, Rb, Ce, and others which are present almost everywhere in the petroleum and bitumens of the vanadium and nickel-vanadium provinces, their concentration coefficients rarely exceed $n \cdot 0.1$, averaging $n \cdot 0.01$. Among these elements, the association Zn-Pb-Cu [Pb-Zn] appears in most crude oils and is related to the high-coking hydrocarbon fractions.

TABLE 3.2

Distribution of rare and disseminated elements in petroleum and natural bitumen in naphthometallogenic provinces of the vanadium and nickel-vanadium types

Districts and regions petroleum and/or bitumens	Age of petroleum-bearing (P) and bitumen-bearing (B) deposits	Concentration of elements	Average content in petroleum and bitumen (wt%)		Average trace element index			Petroleum and bitumen deposit investigated for metal content
			V	Ni	V/Ni	Co/Pb	Co/Cu	
1. Timan-Pechora								
Izhma-Pechora and Timan	D_2, D_3, P (P)	V > Ni > Zn > Sr > Sn > Co > Cu	$28 \cdot 10^{-4}$	$13 \cdot 10^{-4}$	2.1	1.4	2.3	W. Tebuk, Pashinskoye, Dzh'erskoye, Yarega
	D_3–C_1 (B)	V ≥ Ni ≥ Mo ≥ Co ≥ Cu ≥ Cr						Izhem
Pechora-Kolva								
1. Kolva	D_2, C_2–P_1 (P)	V ≥ Ni ≥ Zn ≥ Sr ≥ Sn ≥ CO ≥ Cr	$56 \cdot 10^{-4}$	$37 \cdot 10^{-4}$ (C_2–P_1) $9 \cdot 10^{-4}$ (D_2)	1.5 $3.5 \cdot 10^{-4}$	1.5 2.5	1.9	Usa, Vozey
2. Varandey-Adz'va	D_3, P_2, T (P)	V ≥ Ni ≥ Sr ≥ Cu ≥ Cr ≥ Pb ≥ Mo	$65 \cdot 10^{-4}$	$18 \cdot 10^{-4}$	3.6	–	–	N. Sorokinskoye, Naul'skoye, Toraveyskoye
	C_1 (B)	V > Ni > As > Cr > La > Sr	$29 \cdot 10^{-3}$	$10 \cdot 10^{-3}$	2.9	–	0.5	Talota
3. Shapkino-Yur'yakha	C_2–C_3 (P)	V = Ni ≥ Zn ≥ Sn ≥ Cu ≥ Cr ≥ S						Shapkino, South Shapkino
2. Volga-Ural								
Tatar	D_3, C_1, C_2 (P)	V > Ni > Mo > Sr > Zn > Pb	$40 \cdot 10^{-3}$ (C_1)	$90 \cdot 10^{-4}$	4.4	0.5	0.71	Nurlaty, Bureyka, Yenoruskinskoye,
			$10 \cdot 10^{-3}$ (D_3)	$40 \cdot 10^{-4}$	2.5			Novo-Yelkhovskoye
	P_2 (B)	V > Ni > Zn > Mo > Sr > Pb	$32 \cdot 10^{-3}$	$57 \cdot 10^{-4}$	5.6	0.1	0.89	Tuymetkino, Gorskoye, North Katerginskoye
Melekess	C_1, C_2 (P)	V > Ni > Zn > Sr > Mo > Cu	$55 \cdot 10^{-3}$	$13 \cdot 10^{-3}$	4.3	0.2	0.14	Zimnitskoye, Kondrakovo, Stepnoozerskoye

Table 3.2 cont'd ...

Districts and regions petroleum and/or bitumens	Age of petroleum-bearing (P) and bitumen-bearing (B) deposits	Concentration of elements	Average content in petroleum and bitumen (wt%)		Average trace element index			Petroleum and bitumen deposit investigated for metal content
			V	Ni	V/Ni	Co/Pb	Co/Cu	
Central Volga								
1. Zhiguli	D_3, C_1 (P)	V > Ni > Pb > Zn > Cu	$36 \cdot 10^{-4}$	$17 \cdot 10^{-4}$	2.1	–	–	Syzran, Yablonevyy Ovrag, Zhiguli, Zol'nyy Ovrag
2. Pilyufino	P (P)	V > Ni > Mo > Zn > Sr > Sb	$335 \cdot 10^{-3}$	$62 \cdot 10^{-3}$	5.1	–	0.33	Sadki, Ivanovskoye
Upper Kama	C_1 (P)	V > Ni > Pb > Zn > Cu	$58 \cdot 10^{-4}$	$20 \cdot 10^{-4}$	2.9	–	–	Arlan, Andreyevskoye, Neneuz
Ufimskoye-Orenburg	D_3, C_1 (P)	V ≥ Ni ≥ Zn ≥ Pb ≥ Cu	$51 \cdot 10^{-4}$	$22 \cdot 10^{-4}$	2.3	–	–	Tavtimanovo, Kazanchi, Sergeyevskoye
South Cis-Ural	C_1 P (P)	V > Ni > Pb > Zn > Cu	$53 \cdot 10^{-4}$	$24 \cdot 10^{-4}$	2.2	–	–	Tabyn, Karlinskoye, Ishimbay
3. North Caspian								
Southern North Caspian								
1. Buzachi	J_2, K_1 (P)	V > Ni > Zn > Cr > Co > As > Cu	$14 \cdot 10^{-3}$	$38 \cdot 10^{-4}$	3.7	–	0.7	Karazhanbas, North Buzachi, Kapamkas
2. Ural-Emba	J_2, K_1 (P)	V > Ni > Zn > Cr	$1.8 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	1.1	–	–	Kul'sary, Koschagyl, Makat
	J_2, K_1 (B)	V > Ni > Rb > Cr > La > As	$36 \cdot 10^{-4}$	$10 \cdot 10^{-4}$	3.6	–	–	Kara Murat, Iman-Kara

Table 3.2 cont'd ...

Districts and regions petroleum and/or bitumens	Age of petroleum-bearing (P) and bitumen-bearing (B) deposits	Concentration of elements	Average content in petroleum and bitumen (wt%)		Average trace element index			Petroleum and bitumen deposit investigated for metal content
			V	Ni	V/Ni	Co/Pb	Co/Cu	
3. North Caspian								
Southern North Caspian								
3. South Emba	C_2, P_1, T (P)	V ≥ Ni ≥ Zn ≥ Cr ≥ As ≥ Co	$20 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	2.8	–	–	Prorva, Masabay
Eastern North Caspian	C_1, P_1 (P)	V ≥ Ni ≥ Zn ≥ Cr ≥ Cu ≥ Sn	$39 \cdot 10^{-4}$	$11 \cdot 10^{-4}$	3.5	–	0.005	Kokzhide, Kenkiyak, Zhanazhol, Bozoba
Northern North Caspian	P_1, T (P)	V ≥ Ni ≥ Cr ≥ Zn ≥ As ≥ Co	$6 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	2.0	–	–	West Teplovskoye, Gremyachy, Ul'yanovskoye
4. Middle Ob' area								
Surgut	J, K_1 (P)	V ≥ Ni ≥ Zn ≥ Pb ≥ Sr ≥ Cu	$29 \cdot 10^{-4}$	$7.6 \cdot 10^{-4}$	3.8	0.20	0.66	Ust'-Balyk, N. Surgut, Mamontovskoye, Fedorovskoye
Bartovo	J, K_1 (P)	V ≥ Ni ≥ Zn ≥ Sr ≥ Pb ≥ Cu ≥ Cr	$12 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	3.0	0.29	0.79	Sovetskoye, Sosna
5. Lena-Anabar								
Olenek	ϵ_3, P (B)	V > Ni > Zn > Mo > Cr > Co (La, Ce, Eu, Hf, Au)	$14 \cdot 10^{-3}$	$65 \cdot 10^{-4}$	2.1	–	1.5	Olenek
6. Surkhan-Vaksh								
Surkhan and Vakhsh	(P)	V > Ni > Mo > Cr > Co	$23 \cdot 10^{-3}$	$90 \cdot 10^{-4}$	2.5	–	–	Kokayty, Khaudag, Lyal'-Mikar, Shaambary, Kichik-Bel'

Of basins abroad, the Western Canada, Eastern Venezuela, Maracaibo, Mesopotamian, Gulf of Suez, Adriatic, and the Big Horn, Powder River, and others in the Rocky Mountains on the cratonic complex (C_1–C_3, PT) are among those belonging to the vanadium and nickel-vanadium types of naphthometallogenic provinces (Table 3.4). Among the rare and disseminated elements of petroleum and bitumen, V or V and Ni are predominant in absolute content. On the whole, the average level of concentration of these elements increases from light to heavy high-sulfur crude oils and bitumens. The highest concentrations of vanadium were found in the highly resinous petroleum malthas of the Maracaibo Basin, in particular in the Boscan field (up to 1100 g/t) and in the Bolívar zone (from 156 to 413 g/t); in the heavy oil-maltha of the Orinoco belt of the Eastern Venezuela Basin, from 250 to 490 g/t in the Cerro Negro, Jobo, Zuata, and other fields; and up to 520 g/t in some heavy oil fields in the Mesopotamian basin of Syria (Table 3.4). The nickel content in these heavy oils and malthas usually is 3.5–9.0 times less than that of vanadium and does not exceed 120–150 g/t. In the solid bitumens (asphalt, asphaltite) of stratiform deposits, maximum vanadium and nickel concentrations, up to 200–600 and 150–500 g/t, respectively, were found in the Ouachita (United States) and Adriatic (Albania, Italy) Basins. Higher vanadium concentrations, up to 1200–1650 g/t, are known in the vein asphaltites of Ftéri Mt., Greece and Page, Oklahoma.

A number of heavy oil and bitumen deposits in naphthometallogenic provinces of this type contain large resources of vanadium and nickel (Maracaibo, Eastern Venezuela, and Western Canada).

Of the elements with above-clarke concentrations in the heavy oils and bitumens of provinces of the vanadium and nickel-vanadium types, molybdenum is observed almost everywhere. The average concentration of Mo usually is not more than 5–8 g/t, and only the Scafa, Filettino, Allano, Alatri, and other maltha and asphalt deposits in the the Adriatic basin, in the central part of the Apennines, contain as much as 82–183 g/t of molybdenum. Possibly such strong enrichment in Mo, unknown in other crude oils and bitumens in the world, is related to superposed hydrothermal mineralization.

Compared to the other rare and disseminated elements (Zn, Co, Cu, Cr, Pb, As, Cl, and Ga) that are widespread in petroleum and bitumens, the V-Ni-Mo group of elements, and less often Se, always have high values of their concentration coefficients (Table 3.5).

The following order of concentration of these elements in petroleum and bitumens has been established: I, Mo-V-Ni [Mo-V-Ni-Se] (Big Horn, Powder River, Eastern Venezuela, Maracaibo, and other Basins); II, Mo-V-Ni [Mo-V-Ni-Se] (Western Canada and Adriatic Basins); and III, V-Ni (Western Interior and Mesopotamian Basins). The provinces of the first two subtypes contain almost all known deposits of petroleum and bitumens with above-clarke concentrations of vanadium, nickel, and molybdenum, and have the highest total rare and disseminated element concentrations known in crude oils and bitumens.

Vanadium and nickel-vanadium provinces are confined mainly to basins of a certain tectonic type, such as the basins of old cratons (Volga-Urals and Timan-Pechora, *etc.*), basins of the marginal systems of old cratons (Western Canada, Eastern Venezuela, and Mesopotamian), and basins of intermontane depressions in central massifs (Maracaibo, Adriatic, and Surkhan-Vakhsh).

Nickel and Vanadium-Nickel Provinces

In provinces of the nickel and vanadium-nickel type (Figure 3.1), the concentrations of Ni and, especially, V in both light and heavy oils and bitumens are substantially lower than in vanadium and vanadium-nickel provinces of the first type; only in isolated deposits do the concentrations of these metals exceed the clarke levels.

TABLE 3.3

Concentration coefficients (C_c) of rare and disseminated elements in petroleum and natural bitumen in naphthometallogenic provinces of the vanadium and nickel-vanadium types

Districts and regions of petroleum and/or bitumen accumulation	Age of deposits and composition of accumulations	Concentration coefficients ([ ], main element associations)					Examples of petroleum and bitumen deposits with above clarke concentrations (element-C_c)
		10	10–1.0	1.0–0.1	0.1–0.01	0.01	
1. Timan-Pechora							
Izhma-Pechora	D_2, D_3, P petroleum D_3, C_1 asphalt, asphaltite	– [Re	– V, Ni	[V, Ni] Mo]	– Co, Sc	Zn, Mo, Co Cr, Cu	West Tebuk (V-1.2) Izhem (V-2,5; Ni-1.7)
Kolva	C_2, P_1 petroleum	–	–	[V, Ni]	–	Sn, Zn, Co	–
Vanadey-Adz'va	P_2, T heavy oil C_T asphalt, asphaltite	– [Au	– As], [V, Ni	V, Ni Mo]	Mo Sb, Co, La	Pb, Cu, Cr Cr	– Talota (Au-20; As-3.5; V-2.5; Ni-1.1)
2. Volga-Ural							
Tatar	D_3, C_1, C_2 petroleum and heavy oil	[Re	V, Ni, Mo]	–	[Zn,Pb,Cu]	Co,Cr,Sr	Nurlaty (V-5.4; Ni-1.4; Mo-1.1–7); (V-3.9; Ni-1.2)
	P_2 maltha-high resin petroleum	–	[V	Ni, Mo]	–	[Zn, Pb, Cu]	Gorskoye (V-2.9); N. Karamanly (V-2.6)
Melekess-Abdulino	C_1, C_2 heavy oil	[Re	V, Ni, Mo]	[Zn	Pb, Cu], Cr Cr	Co, Sr	Zimnitskoye (V-8.3; Ni-2.0; Mo-1.1); Pravda (V-6.5; Ni-1.3)
	P_2 maltha, asphalt	[Au, As]	[V	Ni], Pb	Cr, Sc	–	Upper Orlyanskoye (Au-130; As-10.2; V-1.7)
Zhiguli	D_3, C_1 petroleum	–	–	[V, Ni]	–	[Pb, Zn]	–
Pilyugino	P_2 asphaltite (vein)	[V, Mo	Ni], [Sb	Zn]	Ca, Sr	Co	Sadki (V-34.5; Mo-11.0; Ni-6.0; Sb-1.6)

Table 3.3 cont'd ...

Districts and regions of petroleum and/or bitumen accumulation	Age of deposits and composition of accumulations	Concentration coefficients ([ ], main element associations)					Examples of petroleum and bitumen deposits with above clarke concentrations (element-C_c)
		10	10–1.0	1.0–0.1	0.1–0.01	0.01	
3. North Caspian							
Buzachi	J_2, K_1 petroleum	–	[V Au, As	Ni] [Au, As]	Zn, Cu, Ag	Cr, Co	Karazhanbas (V-1.6)
Ural–Emba	J_2, K_1 kirs	[Au	As]	[V, Ni]	Hf, La, Rb	–	Kara–Murat (Au-20; As-2)
South Emba	C_2, P_1, T petroleum	–	[Hg, Sb]	[V, Ni]	Cr, Zn	Co	Prorva (Hg-2.5); Masabay (Sb–5)
Eastern North Caspian	C, P_1 petroleum	–	–	[V, Ni]	Zn, Sb, Cu	Cr, Co	–
4. Middle Ob'							
Surgut and Vartovsk	J, K_1 petroleum	–	–	[V, Ni]	[Pb, Zn]	[Cu,] Co	–
5. Lena-Anabar							
Olenek	$Є_3$, P maltha, asphaltite	Au	[Mo, V	Ni], Zn, As	Ce, Cr, La	Co	Olenek (Au-12; Mo-1.2; V-1.1)
6. Surkhan-Vakhsh							
Surkhan and Vakhsh	P heavy oil	[Re?]	[V, Mo, Ni]	Co, Cr	–	–	Khaudag (V-5.1; Mo-3.0); Kokayty (V-4.0; Ni-2.0)

TABLE 3.4
Rare and disseminated elements contained in petroleum and natural bitumens in the oil and gas basins of foreign countries

Oil and gas basin	Age of deposits and composition of accumulations	Order of concentration of elements	Content of elements in petroleum & bitumens (ppm)		Examples of deposits of petroleum and bitumens with above-clarke concentrations (element content in ppm)	Published source
			V	Ni		
USA						
Los Angeles	N_1–N_2 petroleum, including heavy oil	Ni ≥ V ≥ Co ≥ Mo ≥ Cu ≥ Ca ≥ Se	36–125	84–125	Inglewood (Ni-125)	Hyden (1961)
Great Valley	N_1–N_2 petroleum	Ni ≥ V ≥ Co ≥ Cr ≥ Mo ≥ Pb ≥ Ga	8–82	38–83 (Cd-3.9);	Midway-Sunset Cymric (Nd-23–29)	Shah, Filby and Haller (1970); Valkovic (1978)
Santa Maria	N_1–N_2 heavy oil-maltha	Ni ≥ V ≥ Mo ≥ Cr ≥ Ca ≥ Co ≥ Se	174	130–174	Santa Maria Valley (V-174–280); Ni-174; Mo-4.6; Se-1.4)	
Bighorn	P_2, T petroleum, including heavy oil	V > Ni > Mo > Cu > Cr > Pb	21–106	9–28	–	Ball & others (1960); Valkovic (1978)
	C_1, C_2–C_3, P_1 petroleum, including heavy oil	V ≥ Ni ≥ Zn ≥ Cu ≥ Mo ≥ Cr ≥ Pb	8–117	11–102	Spring Creek (Ni-102)	
San Juan	K_2 light oils	Ni ≥ Cu ≥ Zn ≥ Pb ≥ Co	0.02–0.4	0.7–3.0	–	
Cis-Washita	C petroleum	V > Ni	8–20	2.5–7.0	–	Curiale (1983)
	O asphalt, asphaltite	V > Ni	183–608	200–500	Bigfork (V-540; Ni-200); Pamroy (V-583; Ni-370)	
Powder River	J_3 light oil	V ≥ Ni ≥ Cu ≥ Co ≥ Pb ≥ Cr	0.5–1.5	0.5–1.4	–	Valkovic (1978)
	C_2–C_3, P_1 heavy oil	V ≥ Ni ≥ Zn ≥ Cu ≥ Mo ≥ Pb	72–84	8–72	–	

Table 3.4 cont'd ...

Oil and gas basin	Age of deposits and composition of accumulations	Order of concentration of elements	Content of elements in petroleum & bitumens (ppm)		Examples of deposits of petroleum and bitumens with above-clarke concentrations (element content in ppm)	Published source
			V	Ni		
USA						
Uinta–Piceance	K_2, P_2 light oil	Ni ≥ Cu ≥ V ≥ Pb ≥ Zn ≥ Co	0.02–0.6	0.1–12	–	Ball and others (1960)
	C_2–C_3, T light oil, condensates	Zn ≥ Pb ≥ Ni ≥ V ≥ Cu ≥ Cl ≥ Co	0.02–0.7	0.004–0.8	–	
Western Interior	K_2 petroleum	Ni > V > Cu > Pb > As > Cl	18	22	–	
	K_3 petroleum	V ≥ Ni ≥ Cu ≥ Sr ≥ Zn ≥ Cl ≥ Co	15–18	6–10	–	Hyden (1960)
	C_3–O; C_2–C_3 petroleum, bitumens	V>Ni>Cu>Zn> Co>Cl>Pb	0.3–44	0.1–20	Page (V–1180)	
Canada						
Western Canada	K_1 maltha, high-resin petroleum	V > Ni > Mo > Cr > Ga > Se > Co	145–200	60–75	Athabasca (V-170; Mo-7.2); Cold Lake (V-174; Mo-5.1); Peace River (V-168; Mo-5.3)	Jacobs, Bachelor and Filby (1984)
Venezuela						
Eastern Venezuela	K, ~~P~~$_3$-N high-resin petroleum; maltha	V > Ni > Mo > Cr > Pb > Cu	180–490	72–152	Cerro Negro (V-489; Ni-84); Merey (V-435); Jobo (V-278; Ni-81) Zuata (V-425; Ni-133); Hamaca (V-363); Pilon (V-181; Ni-72)	Abreu and Buenafama (1984); author's data

Table 3.4 cont'd ...

Oil and gas basin	Age of deposits and composition of accumulations	Order of concentration of elements	Content of elements in petroleum & bitumens (ppm)		Examples of deposits of petroleum and bitumens with above-clarke concentrations (element content in ppm)	Published source
			V	Ni		
Venezuela						
Maracaibo	P_2–P_3 heavy oil	V > Ni > Mo > Zn > Cr > Se > As	130–1100	24–150	Boscan (V-1100; Ni-117; Mo-7.8); Bolivar (V-155–413)	Abreu and Buenafama (1984); Hyden (1961); Shah, Filby, and Haller (1970)
Libya						
Sahara–Libyan	K_2, P_1–P_2 petroleum,	Ni > Zn > V > Se > Cu > As	4–8	3–105	(Hg-2.0; Ni-105; Se-1.8)	Shah, Filby, and Haller (1970); Valkovic (1978)
Mesopotamian	T_3, K_2–N_1 petroleum including heavy oil	V > Ni	10–521	5–110	Sfayeh (V-439–521); (V-122–130)	Author's data
Saudi Arabia, Bahrein						
Mesopotamian	J_3, K petroleum	V > Ni > Cd > Zn > Pb > Cr > Cu	2–58	0.5–16	Safaniyah (Cd-2.3); Abqaiq (Ag-0.4)	Ali, Bukharki, and Saleem (1983)
Albania						
Adriatic	N_1 heavy oil	V > Ni > Mo	168–332	33–65	Kuchevo (V-168); Patos (V-285)	Demenkova (1956)
	N_1	V > Ni > Mo	430–521	161	Seleniza (V-521; Ni-161)	

Table 3.4 cont'd ...

Oil and gas basin	Age of deposits and composition of accumulations	Order of concentration of elements	Content of elements in petroleum & bitumens (ppm)		Examples of deposits of petroleum and bitumens with above-clarke concentrations (element content in ppm)	Published source
			V	Ni		
Italy						
	K, P_2 petroleum	V > Ni > Mo > Cr	55–95	30–68	Allano (Mo-19.5)	
	T, K, P_2, N maltha, asphalt	V > Ni > Mo > Cr	45–248	25–109	Scafa (V-248; Ni-109; Mo-82); Filetino (V-196; Ni-154; Mo-171); Allano (V-229; Mo-90; Ni-106)	Colombo and Sironi (1961)
Sicily	T, heavy oil-maltha	V > Ni > Mo > Cr	130–150	90–95	Gela (V-147; Mo-8.4); Nicosia (V-149; Mo-4.8)	
	P_3, -N maltha, asphaltite	Ni > V > Mo > Cr	13–20	70–84	–	
Yugoslavia						
Pannonian	N_1–N_2 light oil	Ni > Zn > V > Cu > Sr	0.6–0.8	3–6.5	–	
West Germany						
Cis-alpine Eastern Molasse	J_1, P_2 petroleum, including heavy oil	Ni > Zn > V > Cu > Co > Se > Cr	0.6–1.7	13–55	Khofolding (Ag-0.32)	Ellrich, Hirner and Stärk (1985)
Western Molasse	T light oil	Ni > Zn > V > Cr > Co > Se		0.2–0.5	0.5–17.5	–
India						
Cambay	P_2 petroleum	Zn > Ni > V > Cr	2.5–5	2.1–35	–	Raghawan and Agrawal (1991)

TABLE 3.5
Concentration coefficients (C_c) of rare and disseminated elements in petroleum and natural bitumen in naphthometallogenic provinces of the vanadium and nickel-vanadium types

Oil and gas basin	Country	Age of deposits	Rare and disseminated elements in order of decreasing concentration coefficient; [ ], main element associations				
			10	10–1.0	1.0–0.1	0.1–0.01	0.01
Vanadium and nickel-vanadium							
Bighorn	U.S.A.	C_1, C_2–C_3, P, T	–	–	[V, Ni, Mo]	–	Cu, Pb, Cr
Powder River		C_2–C_3, P	–	–	[V, Ni, Mo]	Zn, Cu	Pb, Cr
Western Interior		C-0; C_2–C_3 J_3	–	–	[V, Ni]	–	Pb, Co, Zn
Western Canada	Canada	K_1	–	[Mo, V	Ni, Se]	[As, Sb], Cr	Co, Ga
Eastern Venezuela (Orinoco Belt)	Venezuela	K, P_3–N	–	[V, Mo	Ni]	Pb, Cu	Cr
Maracaibo		P_2–P_3, N	–	[V, Mo, Ni	Se, Sb	As], Zn	Cr
Mesopotamia	Saudi Arabia, Bahrein	J_3–K	–	[Cd, Ag]	–	[V, Ni], Pb, Sn	Zn, Cr, Cu
Adriatic	Italy	T, K, P_2, N N_1	[Mo [Mo	V, Ni] V, Ni]	Cr –	– –	– –

Provinces of this type in the former Soviet Union are the South Caspian, Amu Dar'ya, South Mangyshlak, North Ust-Yurt, Fergana, North Caucasus, West Siberian, North Sakhalin, and, in the Baltic region, the Baltic (Figure 3.1).

In the petroleum and bitumens of these provinces, the limits of Ni concentrations are 0.3–82.0 g/t; V, 0.2–60.0 g/t; and Zn, 0.3–63.0 g/t; the concentration ratio, V/Ni, ranges from 0.03 to 1.0, with values of 0.2 to 0.5 predominating (Table 3.6).

Co, Cr, Sr, Cu, Sn, Ga, and Rb are other elements common in crude oil and bitumens, but their content usually is tens or hundreds of times less than the clarke.

Four main associations of elements in petroleum and bitumens, typical of provinces of the nickel type, are distinguished on the basis of maximum values of C_c : I, Ni-Mo (South Caspian, Amu Dar'ya, South Mangyshlak, North Ust-yurt); II, Se-Ni-V (North Caucasus); III, Ni-Sn (Fergana, North Sakhalin); and IV, Pb-Zn [Ni-V] (West Siberian, Baltic) (Table 3.7). The clarke concentrations of these elements usually fall within 0.1–0.01 and rarely are above 0.1. Above-clarke concentrations have been found, but mainly just for elements that are very rare in the Earth's crust, such as Hg, Cd, Au, Ag, Sb, Se, and others. For instance, the heavy crude and maltha of the West Kuban depression are enriched in Au, Cd, Sb, and Se, the concentration coefficients of which are, respectively, 1.0–50.0, 5.5–62.0, 3.2, and 2.0 (Zybza, Akhtyr-Bugundyr, and Adino-Kuban Fields). In some South Mangyshlak fields, above-clarke concentrations of Sb,Hg, and other elements have been observed.

However, the limited and scattered nature of the data on the contents of very disseminated elements so far has precluded a sound prediction of the zones where oil and bitumen deposits enriched in these elements could be found. Moreover, the distribution of Hg, Cd, Sb, Au, Ag, and other elements is extremely uneven within individual deposits, where the concentration of each of those metals in different samples may differ by an order of magnitude or more.

Abroad, there are basins belonging to provinces of the nickel and vanadium-nickel types: California (Los Angeles, Great Valley, and Santa Maria) and the Rocky Mountains (San Juan and Uinta-Piceance) in the orogenic complex (K_2–P_2); and the Sahara-Libyan, Cis-Alpine, and other basins (Table 3.4). On the whole, the crude oils and bitumens of these provinces are less rich in rare and disseminated elements, especially in vanadium, than those of provinces of the first type. In concentration of V, Ni, and other metals, the crude oils and malthas of the vanadium-nickel provinces occupy an intermediate position; the oil and gas basins of California are of this type. Here deposits of heavy oil and maltha containing up to 125–280 g/t of nickel and vanadium are known (Inglewood and Santa Maria Valley Fields). In addition, relatively high concentrations of Hg, Cd, and Se have been found in the petroleum. In the Cymric Field, where Hg concentrations reach 23–29 g/t, Hg is produced as a by-product. In the opinion of some investigators, mercury occurs in petroleum and gases at the nodes of intersections of deep faults and is related to outgassing from the mantle. The mercury potential of California petroleum probably is controlled by the San Andreas fault, with which the distribution of such mercury deposits as New Almaden and New Idria are associated. On the basis of stable maximum values of C_c, the crude oils and malthas of the California basins have the following elemental associations: Hg-Cd and Se-Ni-V-Mo [Se-Mo-Ni-V].

In the crude oils and bitumens of the orogenic complexes of the Rocky Mountain oil and gas basins (San Juan and Uinta-Piceance), Ni, Cu, Zn, and Pb predominate in absolute rare element content; the Ni concentration in the petroleum is not more than 12 g/t, and that of vanadium measures in tens of grams per ton. It is noteworthy that even in the vein asphaltite deposits, such as Cowboy,

TABLE 3.6
Distribution of rare and disseminated elements in petroleum and natural bitumen in naphthometallogenic provinces of the nickel and vanadium-nickel types

Districts and regions petroleum and/or bitumens accumulation	Age of oil- and gas-bearing (P) and bitumen-bearing (B) deposits	Order of concentration of elements	Average content of elements in petroleum and bitumens (10^{-4} wt%)			Trace element indicators (average)			Petroleum and bitumen deposits investigated for metal content
			Ni	V	Zn	V/Ni	Co/Pb	Co/Cu	
1. South Caspian									
Aspheron	N_1–N_2 (P)	Ni ≥ V ≥ Zn ≥ Co ≥ Pb ≥ Mo	5.0	0.5	0.5	0.10	0.7	0.3	Surakhany, Sabunchi, Gryazevaya Sopka, Neftyannyye Kamin, Banka Darvina
West Turkmenian	N_2 (P)	Ni > V > Zn > Sr > Cu > As	4.3	0.3	–	0.07	–	0.7	Dagadzhik, Keymir, Kum-Dag, Kotur-Tepe
2. Amu Dar'ya									
Bukhara-Khiva	J_2–K (P)	Ni > V > Zn > Sr > Cu > As	0.7	0.5	0.3	0.7	1.0	0.6	Akdzhar, Kyzylravat, Mubarek, Shurtepe, Karabair
3. South Mangyshlak									
Zhetibay-Uzen'	J_1–J_3 (P)	Ni > Zn > Sr > V > Cu > Pb	5.3	0.4	1.5	0.08	0.5	0.4	Zhetibay, Uzen', Tasbulat, Tenge
	P–T (P)	Ni > Zn > Pb > Sr > V > Cu	12.5	0.2	2.3	0.02	0.1	0.4	Uzen'
4. North Ust-Yurt									
Chumshty-Vasay	J_2 (P)	Ni > Zn > Cu > Sr > Pb > Sn	0.9	0.01	0.08	0.01	0.02	0.1	Arstan

Table 3.6 cont'd ...

Districts and regions petroleum and/or bitumens accumulation	Age of oil- and gas-bearing (P) and bitumen-bearing (B) deposits	Order of concentration of elements	Average content of elements in petroleum and bitumens, (10^{-4} wt%)			Trace element indicators (average)			Petroleum and bitumen deposits investigated for metal content
			Ni	V	Zn	V/Ni	Co/Pb	Co/Cu	
5. Fergana									
North Fergana and South Fergana	₽ (P)	Ni > V > Zn > Sn > Sr > Cr	1.5	0.75	0.5	0.5	3.0	0.7	Shor-Su, Mayli-Su, Andizhan, Tash-Ravat
6. North Caucasus									
Indolo-Kuban	₽–N (P,B)	Ni > V > Zn > Co > Cu	8.8	1.6	1.0	0.18	–	–	Akhtyr-Bugundyr, N. Krymskoye, Zybza, Abino-Kuban
7. Baltic									
Krasnoborsk	$Є_2$, O_3 (P)	Ni ≥ V ≥ Zn ≥ Cr ≥ Sn ≥ Sr	1.3	1.2	0.8	0.9	–	2.5	Isakovo, Ushakovo, Krasnoborsk, Gusevskoye
Gardzhay	$Є_2$ (P)	Ni ≥ Zn ≥ Cu ≥ V ≥ Sr ≥ Cr	0.8	0.3	0.5	0.3	–	0.09	Shyuparyay, South Shyuparyay, Deglyay
8. West Siberian									
Pri-Ural	J_2, K_1 (P)	Ni > Zn > V > Pb > Sr > Sn	9.4	5.8	6.3	0.6	0.06	1.0	Mulym'ya
Vasyugan	J_3 (P)	Ni > Zn > V > Pb > Cu > Sr	3.1	0.5	2.3	0.18	0.2	0.5	Okhtsur'yev, Central Vasyugan
9. North Sakhalin									
Okha	N_1–N_2 (P)	Ni > V > Zn > Sr > Ga > Cu	2.5	0.8	0.5	0.3	0.2	0.4	Okha, Bol. Ekhabi, Katangli
	N–Q (B)	Ni ≥ Zn ≥ Pb ≥ V ≥ Ga	5.9	1.9	–	0.3	0.2	0.4	Nutovo, Okha

TABLE 3.7
Concentration coefficients (C_c) of rare and disseminated elements in petroleum and natural bitumen of naphthametallogenic provinces of the nickel type

Districts and regions of petroleum and/or bitumen accumulation	Age of deposits and composition of accumulations	Concentration coefficients; [ ], main element associations					Examples of petroleum and bitumen deposits with above-clarke concentration coefficients (C_c)
		>10	10-1.0	1.0-0.1	0.1-0.01	<0.01	
1. South Caspian							
Aspheron	N_1-N_2 petroleum	–	–	–	[Ni, Mo]	Co, Zn, V	–
West Turkmenian	N_2 petroleum	–	–	–	[Ni, Mo]	Sn, Co, Zn	–
2. Amu Dar'ya							
Bukhara-Khiva	J_2-K petroleum	–	[Au	Ag, As]		[Ni, Mo]	Akdzhar (Ag-1.1); Karabair (Au-3.3)
3. South Mangyshlak							
Zhetybay-Uzen'	J_1-J_3	–	–	–	[Ni, Mo], Zn [Pb, Cu]	Sn [Pb, Cu]	–
P-T petroleum					[Ni, Mo]	[Zn, Pb], Co	
4. North Ust-Yurt							
Chumshty-Vazay	J_2 petroleum	–	–	–	Ni, Mo	Cu, Co, Sn	–
5. North Caucasus							
Indolo-Kuban	P-N heavy oil-maltha	Cd, Au	Sb, [Se	Ni	V], Zn	Co, Cu, Sc, Cr	Zybza (Au-up to 50); Akhtyr-Bugundyr (Cd-5.5-62); Abino-Kuban (Sb-up to 3.0)
6. West Siberian							
Pri-Ural	J_2-K_1 petroleum	–	–	[Pb	Zn], [Ni, V]	Sn, Cu, Cr	–
Vasyugan	J_3 petroleum	–	–	–	[Pb, Zn]	[Nk, V], Cu	–
7. North Sakhalin III							
Okha	N_1-N_2 petroleum	–	–	–	[Ni, Sn]	Zn, V, Pb, Cr, Cu	–

Bonanza, and Capitol Reef that are common in the Uinta-Piceance basin, the V and Ni contents do not exceed 13–20 g/t, and Mo, 1.5 g/t (Erickson, Myers, and Horr, 1954), whereas in vanadium-type provinces, such vein formations as a rule have high metal concentrations.

Maximum values of C_c for Ni, Cu, and Zn in the petroleum and bitumens of these provinces are only $n \cdot 0.1$ (Table 3.8). In some petroleum and bitumen deposits of provinces of the nickel type (Sahara-Libyan and Cis-Alpine), concentrations of Hg, Se, and Ag that are high relative to the clarke have been found, as has been observed in provinces of the same type in the former Soviet Union, where Au, Cd, and Sb have been found in addition.

The oil and gas provinces of this metallogenic type occur mainly on young platforms and their marginal systems, in epicratonic orogens, and in graben synclinoriums.

Zinc Provinces

The crude oils and bitumens that are poorest, both in total metal content and in concentration of individual elements, are those of the zinc-type provinces.

In the former Soviet Union, the Yamal-Tazovsk, East Siberian, and Lena-Vilyuy Provinces, among others, are of this type (Figure 3.1). The predominant elements in their petroleum and bitumens are Zn, Pb, and Cu, concentrated not only in the residues but also in the high-coking fractions. The average concentration of Zn in petroleum (according to the samples studied) falls in the range of 0.2 to 6.5 g/t; of Ni, 0.08 to 1.2 g/t; and of V, 0.03–0.5 g/t (Table 3.9). It is significant that even in the heavy oils in these provinces, the concentrations of V and Ni seldom exceed $n \cdot 10^{-4}$ wt% (Russkoye and other heavy oil fields in northern West Siberia, *etc.*). Data on the fractionation of these petroleums (Nadirov, Koronova, Kam'yanov *et al.*, 1984) show that the main concentrators, the resins and asphaltenes, contain several times less metals than the same petroleum fractions from other types of provinces. In particular, the vanadium contents of these fractions in asphaltenes and resins from the Russkoye Field (zinc province) are 76.6 and 35.2 g/t respectively; in asphaltenes and resins from the Samotlor and West Surgut Fields (nickel-vanadium province) they are 410–519 and 247–366 g/t, respectively; and in the asphaltene fraction of petroleum of the Khaudag deposit (vanadium province), the vanadium content reaches 1550 g/t.

Low V and Ni contents also are observed in the asphaltite, asphalt, and maltha that form accumulations in many regions of the Lena-Tungusska Province. For instance, study of asphaltite and asphalt of the Turakhan area (Nizhnyaya [Lower] and Sukhaya [Dry] Tungusska Rivers) showed that the V content is not more than 20 g/t and the Ni, not more than 10–65 g/t; in asphaltite from the Middle Cambrian limestones of the Olenek River, the nickel content is about 30 g/t. The V/Ni ratio ranges from 0.02 to 0.20 in light oils and from 0.4 to 0.8 in heavy oils and asphaltic bitumens.

On the basis of stable maximum values of the concentration coefficients in petroleum and bitumens of naphthometallogenic provinces of this type, two main element associations are distinguished: I, Zn-Pb [Pb-Zn] and II, Zn-Pb-Cu [Zn-Cu-Pb] (Table 3.10). The C_c values for Zn, Pb, and Cu usually range from 0.1 to 0.01; other elements that accumulate in the petroleum and bitumens, such as Ni, Mo, V, Cu, Sr, and Cr, have C_c values less than 0.01.

In provinces of the zinc type in the former Soviet Union, no above-clarke concentrations of rare and disseminated elements have been found in the deposits of petroleum and bitumen that have been tested.

TABLE 3.8
Concentration coefficients (C_c) of rare and disseminated elements in petroleum in naphthometallogenic provinces of the nickel, vanadium-nickel, and zinc types

Oil and gas basin	Country	Age of deposit	Rare and disseminated elements in order of decreasing concentration coefficients; [ ], main associations of elements				
			10	10–1.0	1.0–0.1	0.1–0.01	0.01
Nickel and vanadium–nickel							
Los Angeles	USA	N_1–N_2	–	[Se, Ni	V, Mo]	Co, Cu, Cr	Ga
Great Valley		N_1–N_2	[Hg	Cd]	[Ni, V, Mo]	Co, Cr, Ga	Pb
Santa Maria		N_1–N_2	–	[Se, Mo, Ni, V]	–	Cr, Co, Ca	–
San Juan		K_2	–	–	–	[Ni, Cu, Zn]	Pb, Co, V
Uinta-Piceance		K_2, P_2	–	–	[Ni, Cu]	Pb, Zn	Co, V
Sahara-Libya	Libya	K_2, P_1–P_2	–	Hg, [Se, Ni]	Zn, Sc	[Sb, As]	Co, Cr, Cu
Cis-alpine	W. Germany	J_2, P_2		Ag	[Ni, Sc]	Cu, Co, Zn	V, Cr
Zinc							
Uinta-Piceance	USA	C_2–C_3, T	–	–	[Zn, Pb]	–	Ni, Cu, Co, V
Cambay	India	P_2	–	–	[Zn	Ni]	V, Cr

TABLE 3.9

Distribution of rare and disseminated elements in petroleum in napthometallogenic provinces of the zinc type

Districts and regions of petroleum and bitumen accumulation	Age of petroliferous (P) and bitumen-bearing (B) deposits	Order of concentration of elements	Average content in petroleum and bitumens (10^{-4} wt%)			Trace element ratios (average)			Oil fields investigated for metal content
			Zn	Ni	V	V/Ni	Co/Pb	Co/Ca	
1. Yamal-Tazovsk									
Yamal	K_1 (P)	Zn ≥ Sr ≥ Ni ≥ V ≥ Pb ≥ Cr ≥ Cu	4.4	0.19	0.09	0.48	0.5	0.76	Novyy Port
Pur-Tazovsk	K_2 (P)	Zn ≥ Sr ≥ Ni ≥ V ≥ Pb ≥ Cr ≥ Cu	0.5	0.45	0.2	0.44	0.3	0.80	Tazovsk
2. Lena-Tungusska									
Anabar	$Є_1$ (P)	Zn > Cu > Ni > Cr > Sr > V > Pb	6.4	0.73	0.38	0.52	0.20	0.003	Kenelikan Springs
Nepa-Botuobuya	Vmt_1–$Є_1$ (P)	Zn > Ni > Cu > Pb > Sn	3.5	1.2	0.1	0.08	0.40	0.01	Markovskoye, Krivolukskoye, North Markovskoye, Yaraktinskoye
3. Lena-Vilyuy									
Vilyuy	T_1, J_1, J_3 (P)	Zn > Cu > Ni > Sr > Pb > Sn > V	0.90	0.12	0.015	0.12	–	0.02	Bergeinskoye, Tolon, Middle Vilyuy
	$₽_2$ (P)	Zn > Cu > Ni > Sr > Pb > Cr > V	5.4	0.75	0.13	0.17	–	0.02	Nedzheli
4. East Kamchatka									
E. Kamchatka	₽–N (P)	Zn > Ni > V	0.6	0.08	0.03	0.37	–	–	Bogachevka, Uzon (springs)
5. Anadyr									
Izmennaya	N (P)	Zn ≥ Ni ≥ Cu ≥ V ≥ Ti ≥ Cr ≥ Pb	0.26	0.09	0.026	0.29	0.77	0.13	Izmennaya

TABLE 3.10

Concentration coefficients (C_c) of rare and disseminated elements in petroleum in naphthometallogenic provinces of the zinc type

Districts and areas of petroleum accumulation	Age of deposits and composition of accumulations	Concentration coefficients; [ ], main element associations				
		10	10–1.0	1.0–0.1	0.1–0.01	0.01
Nickel and vanadium–nickel						
1. Yamal'–Tazovsk						
Yamal'	K_1 petroleum	–	–	–	[Zn	Pb], [Mo, Ni, V]
Pur–Tazovsk	K_2 petroleum	–	–	–	–	[Pb, Zn], [Ni, Mo, V]
2. Lena–Tungusska						
Anabar	$Є_1$ petroleum	–	–	–	[Zn, Cu	Pb], Ni, Cr, V, Co
Nepa-Botuobuya	V–$Є_1$ petroleum	–	–	–	[Zn, Pb, Cu], Sn	[Mo, V, Ni]
3. Lena–Vilyuy						
Vilyuy	T_1, J_1, J_3 petroleum	–	–	–	–	[Zn, Cu, Pb], Sn, Ni, Mo
P_2 petroleum	–	–		[Zn	Pb, Cu]	Ni, Sn, Mo, Cr

Of foreign basins, zinc provinces include the cratonic complex of the Uinta-Piceance and the Cambay Basins, which contain Zn, Pb, Ni, Cu, V, Cr, Ce, Co, and other rare and disseminated elements in their petroleum. The clarkes of the concentration of the first elements in the series (Zn, Pb, Ni) usually are less than $n \cdot 0.1$, and of the rest, less than 0.01 (Table 3.8). For instance, the content of Ni in the Pennsylvanian deposits of the Uinta-Piceance Basin is not more than 0.15–0.83 g/t; Zn, 0.33–1.20 g/t; and V, 0.02–0.70 g/t. In the Cambay Basin, the petroleum contains 1.6 to 21.6 g/t Zn, 2.1 to 35.0 g/t Ni, and 2.5 to 5.0 g/t V. It is noteworthy that in the heavy oils of the Bekrol Field (0.956 g/cm^3), the maximum concentration of Ni (35 g/t) is found where Zn is absent. No above-clarke concentrations of rare elements were found in the petroleum of these provinces.

Zinc provinces as a rule are confined to very deeply subsided cratonic structures or basins, where the oil source formations are characterized by high stages of catagenesis of organic matter, especially in basins of marginal depressions like the Cis-Ural, Cis-Verkhoyansk, Cis-Carpathian, and others.

3.3 GEOLOGICAL-GEOCHEMICAL CONDITIONS GOVERNING THE METALLOGENIC SPECIALIZATION OF OIL AND GAS BASINS

Finding the factors that determine the metallogenic specialization of oil and gas basins and the level of concentration of rare elements is linked to the solution of problems of the sources, paths of accumulation, and forms of occurrence of the rare elements in petroleum and bitumens. So far,these problems have not been unambiguously solved. Existing hypotheses (Yen, 1975; Aleshin, Glukhov, Kocheva, and Kam'yanov, 1984; Nadirov, Korova, Kam'yanov *et al.*, 1984; Chakhmakhchev, Punanova, and Lositskaya, 1984; and Goldberg, Kaplan, and Ponomarev, 1986) recognize the primary biogenic nature of the rare elements, inherited by the petroleum from organic matter in the source rocks. The possibility also exists of secondary introduction of at least some of the metals, such as V, Au, Re, U, Cd, La, Sc, Sr, Be, Mo, and others, into the petroleum as a result of its reaction with inorganic components of the rocks and waters, as well as by various biochemical processes.

As our investigations have shown (Goldberg, 1989a,b, 1991), the metallogenic specialization of oil and gas basins is governed by the following factors: (1) grades of catagenesis in the main zone of petroleum formation; (2) chemical composition of the original bitumoids ("micropetroleum") and petroleum and, in particular, the content of high molecular weight compounds; and (3) the possibility of enrichment of petroleum in rare and disseminated elements over vast zones of infiltration.

Analysis of data on the distribution of rare and disseminated elements in the oil source rocks of various basins shows that the so-called domanikite facies, the highly carbonaceous marine planktonogenic deposits (Figure 3.2), contains a rare element association similar to the one found in metalliferous petroleum and bitumens (Mo, Re, Se, Cd, Bi, V, As, Ag, Au, Sb, Ni, Zn, Cu, and Co). These deposits accumulated in uncompensated ("starved"), relatively deepwater basins with extremely low sedimentation rates (from 1 to 6 m/Ma), which promoted prolonged processes of absorption of metals from sea water by active organic matter in early diagenesis, leading to the formation of large geochemical anomalies (Goldberg, Mitskevich, Lebedeva, and Nazarov, 1991; Goldberg, Miskevich, Lebedeva, and Solodukhin, 1991).

In addition, the possibility of realizing the ore-source bed potential of the oil-producing domanikite formations depends on the conditions of generation of the petroleum and, primarily, on the degree of catagenesis of the organic matter. Analysis of the distribution of rare and disseminated elements in bitumoids and petroleum associated with domanikites with PK_2 to MK_3 levels of

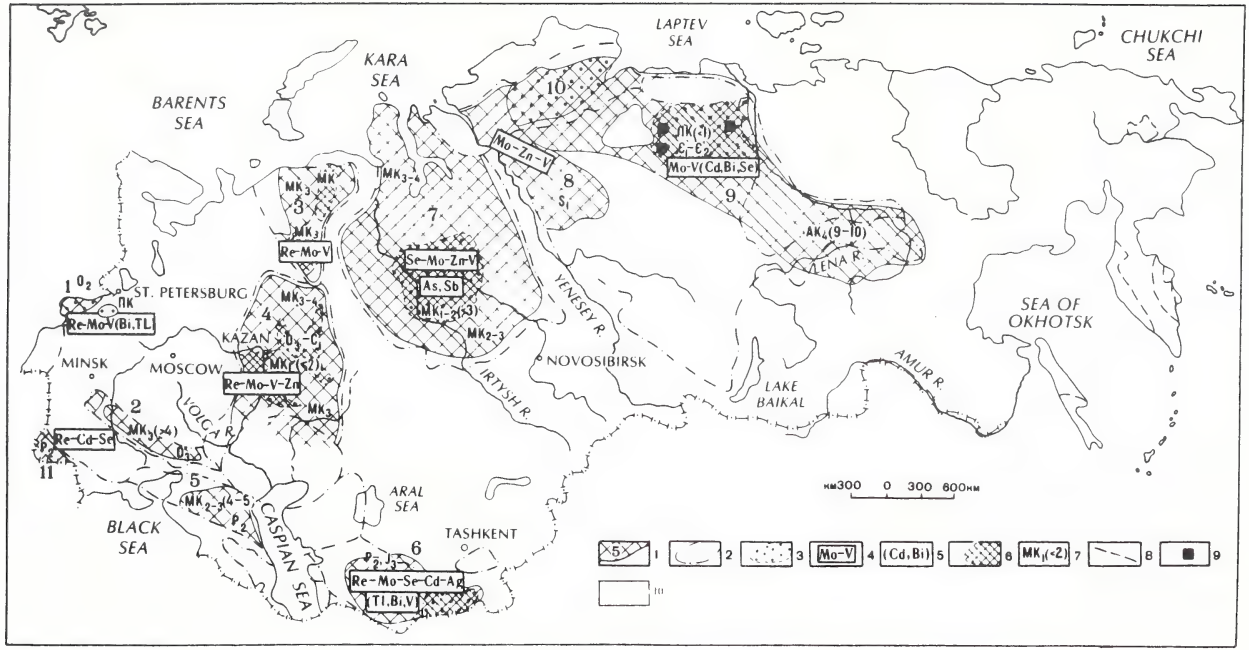


FIGURE 3.2

Metallogenic map of domanikites and regionalization of zones of generation of metal-containing petroleum in sedimentary basins of the former Soviet Union [Compilers: I.S. Goldberg and G.V. Lebedeva]

1 – Sedimentary basins containing domanikites: 1. Baltic; 2. Dnepr-Donetsk-Pripiat; 3. Timan-Pechora; 4. Volga-Urals; 5. North Caucasus; 6. Central Asia; 7. West Siberian; 8. Tungusska; 9. Yudoma-Olenek; 10. Igarka-Norilsk; 11. Carpathians

2 – Limits of petroliferous basins

3 – Domanikites rich in organic matter and trace elements

4 – Basic metallogenic associations, in order of decreasing elemental concentrations

6 – Possible generation zones of metalliferous petroleum and bitumen

7 – Grades of catagenesis of the dispersed organic matter, with depth (m) in parentheses

8 – Boundaries of oil and gas regions

9 – Domanikites with metal-bearing bitumen

10 – Areas where domanikites are absent

transformation of organic matter showed that as catagenesis increases: (1) the contents of V, Mo, Ni, Cr, Co, Sc, Ag, Sb, and other rare and disseminated elements bound in high molecular weight compounds decrease; (2) the concentration of metalloporphyrins decreases, beginning with the MK_2 stage; and (3) the relative proportions of Pb, Zn, Cu, Hg, and other rare and disseminated elements present in the oil and high-boiling fractions increase (Table 3.11).

According to the scale of catagenesis of organic matter (Parparova and Zhukova, 1990), the boundary values of catagenesis of the petroleum-producing domanikite deposits can be tentatively established: (1) PK_3–MK_2 (vanadium and nickel-vanadium); (2) MK_2–MK_3 (nickel and vanadium-nickel); and (3) above MK_3 (zinc).

This conclusion is confirmed by calculations of the incorporation of metals into bitumoids from the organic matter of the source rocks at different grades of catagenesis (Table 3.12; Figure 3.3). For instance, in the Domanikite Formation, at grades PK_3–MK_1, 83 percent of the V, 71 percent of the Ni, 11 percent of the Mo, 9 percent of the Zn, 8 percent of the Ag, and 6 percent of the Cr are incorporated in bitumoids; at grades MK_2–MK_3 in the Kumsk Formation, 3 percent of the V, 22 percent of the Ni, 0.5 percent of the Mo, 0.4 percent of the Co, 32 percent of the Zn, and 0.8 percent of the Cr are so incorporated. As catagenesis of the organic matter increases, the content of oil fractions in bitumoids increases, from 20 to 60 percent, and the content of asphaltenes and other high molecular weight hydrocarbons decreases, in the case of the asphaltenes from 30 to 6 percent.

Therefore, in basins with a high degree of catagenesis of the organic matter, in domanikoid source rocks, the original petroleum is impoverished both in total rare element content and in concentration of elements such as V and Ni, which could be useful by-product components.

Petroleum formed from rocks with humic types of organic matter, as well as from rocks sharply depleted in V, Ni, Mo, and other elements, should be similar in metallogenic respects.

At the same time, basins characterized by the presence of petroleum-producing domanikite strata in the section, which entered the main phase of petroleum formation in relatively early stages of catagenesis (PK_3-MK_1), contain primary petroleum with relatively high concentrations of these organophilic elements. A favorable point, which causes an acceleration of processes of petroleum formation and promotes more complete migration of rare and disseminated elements from organic matter into micropetroleum, is the siliceous-carbonate composition of domanikite, in which organic matter is not closely bound, crystallochemically, to the main matrix of the rock (see Chapter 5). Therefore, basins with this combination of indices, such as the Volga-Urals, Surkhan-Vakhsh, and part of the Timan-Pechora, are very promising for finding metalliferous petroleum and natural bitumens, primarily V, Ni, and Re.

In the West Siberian Basin, where the metalliferous domanikite petroleum source rock, the Bazhenovo Formation, containing Se, Mo, U, Sb, V, and Ni, is present in the section, the petroleum is impoverished in those elements. The sharp discrepancy between the rare and disseminated element concentrations in the domanikites and in the petroleum apparently is governed by the composition of the rocks of the Bazhenovo Formation, in which the organic matter forms stable organomineralic compounds with the inorganic part of the rock. Therefore, the processes of generation of petroleum here began at higher grades of catagenesis of organic matter (MK_1–MK_2) than in the Domanik Formation of the Russian craton, resulting in a lighter composition of the bitumoids and relatively low content of the metals V, Ni, and Mo in the asphalt-resin fractions. Judging from the rare and disseminated element composition of the petroleum of other areas of the West Siberian Basin, in which the percentage of elements such as Zn, Pb, Cu, and Sr is higher, the processes of petroleum

TABLE 3.11
Concentration of elements in bitumoids from deposits of the domanik type

Age, formation	Stage of catagenesis	Trace element content (g/t)													
		V	Zn	Ni	Mo	As	Se	Cr	Co	Sb	Sc	La	Cs	Ag	Au
$Є_1$–$Є_2$ Kuonamka	PK_2	1200	40	70	97	23	3	30	20	–	1.5	–	–	0.2	–
D_3, Domanikite	PK_3–MK_1	1410	116	310	4.2	3.5	–	5.8	0.4	–	0.15	–	–	0.2	–
J_3–K_{1V}, Bazhenovo	MK_1–MK_2	230	91	19	0.2	0.9	0.08	2.2	0.03	0.3	0.008	0.07	0.05	0.02	0.003
P_2 Kumsk	MK_2–MKv	9.5	10.5	12.5	0.1	5.7	0.01	0.5	0.02	–	0.007	0.06	0.002	–	0.001

TABLE 3.12

Quantitative relationships among trace elements in bitumoids and petroleum from the Domanik and Bazhenovo formations

Trace element	Volga-Urals area, catagenesis PK_3-MK_2			Central Volga area, catagenesis MK_1-MK_2		
	Quantitative relationships of elements (%)					
	bitumoid / rock (Domanik)	bitumoid / petroleum	petroleum / rock (Domanik)	bitumoid / rock (Bazhenovo fm.)	bitumoid / petroleum	petroleum / rock (Bazhenovo fm.)
V	83.5	8.5	7.1	42.5	12.6	5.3
Ni	81.0	11.5	9.8	44.0	5.8	2.6
Mo	18.0	13.0	2.5	0.6	1.5	0.01
Zn	–	–	–	1.0	12.8	0.2
Cu	5.1	5.5	0.3	10.0	1.5	0.2
Pb	11.5	18.2	2.1	4.5	35.0	1.6
Co	3.2	5.0	0.2	0.1	4.2	0.04
Cr	4.1	4.0	0.3	0.7	1.7	0.01
Ti	1.0	4.5	0.0–5	0.1	0.8	0.001
Zr	5.3	1.0	0.05	0.1	5.0	0.001
Sr	4.5	12.0	0.5	0.07	6.9	0.004
Ga	2.1	10.0	0.2	0.3	–	–
Sc	1.3	3.3	0.05	0.7	0.2	0.1
Be	1.0	3.3	0.03	–	–	–

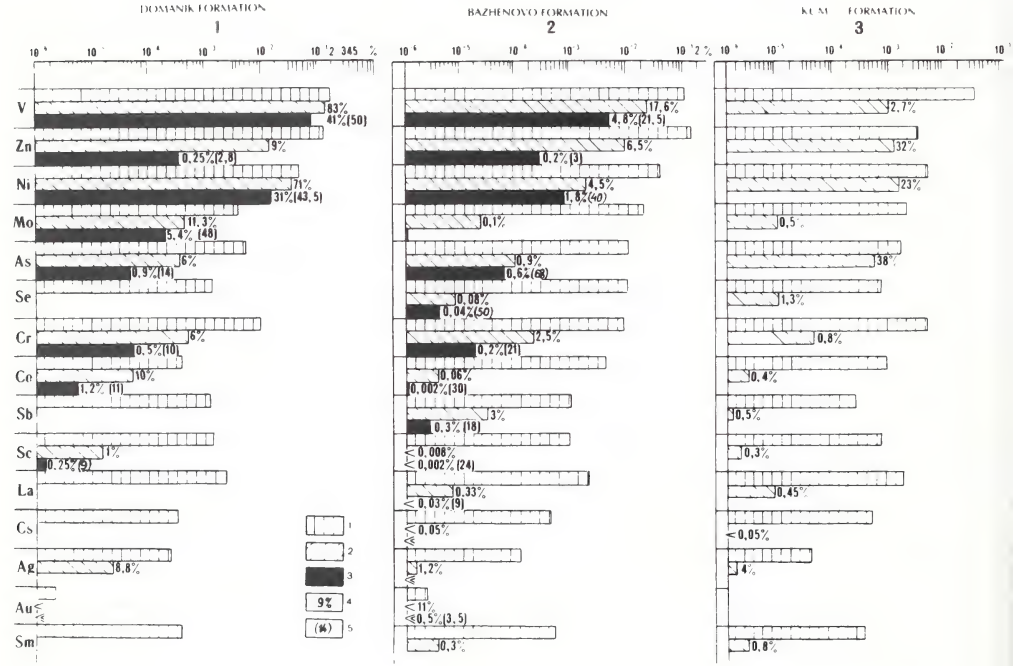


FIGURE 3.3

Correlation of metal concentrations in petroleum, chloroform-extracted bitumen, and source rocks (domanikites) at different stages of catagenesis of the disseminated organic matter

1 – Domanikite
2 – Chloroform-extracted bitumen
3 – Petroleum
4 – Metal concentration showing percent associated with domanikite
5 – Metal concentration showing percent associated with chloroform-extracted bitumen
Domanik Formation, D_3: Volga-Urals, MK_1 stage of catagenesis at depth to 2 km
Bazhenovo Formation, J_3: middle pre-Ob, MK_1–MK_2 stage of catagenesis at depth to 3 km
Kum Formation, P_2: Cis-Caucasus, end of MK_2 stage of catagenesis at depth of 4.4–4.8 km

formation occurred here at higher grades of catagenesis than in the Middle Ob' region. It is noteworthy that even in the heavy oils of northern West Siberia (the Russkoye and other Fields), the contents of V and Ni are only 35.2 and 76.6 g/t, respectively, in the resins and 76.6 and 178 g/t in the asphaltenes. For comparison, the V and Ni contents in the resins from Samotlor petroleum are 247 and 53 g/t and in the asphaltenes 519 and 268 ppm, respectively. At the same time, there is a decrease in the Zn content, from 61.7 g/t in the asphaltenes from Russkoye petroleum to 12.1 g/t in asphaltenes from Samotlor petroleum (Nadirov, Korova, and Kam'yanov, 1984). That mode of partitioning of the rare and disseminated elements is reflected in the metallogenic regionalization of the petroleum of the West Siberian basins, the central part of which (Middle Ob' oil and gas province) belongs to the vanadium-nickel type, the eastern and southern parts (Cis-Ural and Vasyugan oil and gas provinces) to the nickel type, and the northern part (Yamal'and Pur-Tazovsk oil and gas provinces) to the zinc type.

The above data show that the inverse problem — determining probable source rocks and ascertaining the conditions of petroleum formation — can be solved on the basis of the rare and disseminated element composition of the petroleum. In particular, on the basis of the rare and disseminated element composition of the petroleum of the Nepa-Botuobuya zone of the Lena-Tungusska basin, the absence of a genetic relationship between the rare and disseminated elements and the deposits of the Kuonamka Formation has been fairly definitely established. The similarity of the petroleum of the upper Permian, Triassic, and Jurassic deposits of the Vilyuy syneclise and the Vendian-Cambrian deposits of the eastern part of the Siberian craton may indicate that all the petroleum came from the same source rock.

Thus, the difference in the conditions of petroleum formation in different sedimentary basins, and the oil and gas-bearing complexes in the basins is reflected in the metallogenic specialization of the petroleum and natural bitumen.

For many petroleum source rocks, a correlation has been observed between the content of vanadium and vanadyl porphyrins in the petroleum. According to Belokon' (1987), the maximum concentration of vanadyl porphyrins (more than 600 g/t) is found in petroleum genetically related to highly carbonaceous sapropelic formations (domanikites) at low stages of catagenesis (not more than MK_1-MK_2); this is confirmed by the predominance in them of tetrapyrroles of DPEP type. Porphyrin-rich petroleum is typical of the richest vanadium-bearing petroleum parent rocks of the world (Volga-Urals, Surkhan-Vakhsh, Adriatic, and Maracaibo Basins). The paragenesis of porphyrin-rich and vanadium-rich crude oils apparently is governed by a common source, the content of vanadyl porphyrins in domanikites reaching a few thousand mg per 100 g of bitumoid, and by the ability of vanadium complexed with porphyrins to be dissolved in hydrocarbons and carried considerable distances. The ability of vanadium to migrate in a dissolved state is reduced as the degree of catagenesis increases to MK_3 and above, when the main nucleus of the pigments decomposes.

Not only catagenesis of the source rocks but also the genetic type of organic matter greatly affect the distribution of metalloporphyrins as well as of "non-porphyrin" metals in petroleum. If humic organic matter is predominant in a petroleum, the content of metals (V and Ni) bound to porphyrins decreases, while the percentage of nickel complexes increases as, for example, in the South Caspian, Fergana, North Kuban, and other Basins.

The metallogenic type of a number of oil and gas provinces and districts is also governed by superposed rare and disseminated element associations related to the introduction of metals from the catchment areas of infiltrating fresh or slightly mineralized waters. For instance, in the vast zones of

infiltration in the Maracaibo, Eastern Venezuela, and Barinas-Apure Basins, which are adjacent to outcrops of the vanadium-bearing crystalline rocks of the Guiana shield and Andes fold structures, petroleum and bitumens are sharply enriched in vanadium.

As a result of model experiments, Chakhmakhchev, Punanova, and Lositskaya (1984) demonstrated that when petroleum reacts with slightly mineralized water (up to 5 g/l) containing $n \cdot 10^{-5}$ percent vanadium, there is a steady increase in the vanadium concentration, up to $n \cdot 10^{-2}$ percent. The amount of vanadium absorbed is 0.3–51.5 mg per 100 g of petroleum, which indicates a 1.3 to 10-fold increase in native V mineralization. The relationships between [V] and [A+Rm], [Ni], and [S] that we calculated from analytical data for secondarily vanadiferous crude oils and bitumens show that they are exponential functions, in contrast to petroleum and bitumens of the organophilic type, where the the relationships between the same components are linear.

3.4 GENETIC TYPES OF METALLIFEROUS HEAVY OIL AND BITUMEN DEPOSITS

On the basis of the processes of concentration of metals in heavy oils and bitumens, a genetic classification of these metalliferous deposits has been worked out (Goldberg, 1989a,b, 1990, 1991) (Table 3.13).

Two main types of ore concentrations in heavy oils and bitumens may be distinguished: (1) organophilic, in which the source of rare elements is the ore component of the organic matter of oil-producing domanikite associations; and (2) secondarily concentrated, related to the sorption of metals from high molecular weight compounds by heavy oils and bitumens from infiltrating waters and hydrothermal solutions (concentration at physicochemical barriers).

The Organophilic Type of Metalliferous Deposit

Three subtypes of organophilic ore concentrations, restricted mainly to petroleum source rocks of the vanadium and nickel-vanadium types, are distinguished on the basis of the concentration of the metals.

The early catagenetic subtype

The early catagenetic subtype is produced as a result of the mobilization of metals (V, Ni, Mo, Re, and Cr) from the organic matter of immature source domanikites, in which catagenesis is not higher than MK_1 and Ro is less than 0.60 percent. This occurs during early generation of originally heavy high-cyclic petroleums and liquid malthas enriched in high molecular weight and heteroatomic compounds, the so-called immature petroleums.

The characteristics of the early catagenetic subtype are: (1) alkane-arene or arene-alkane, with a predominant content of the benzene-extractable fraction of the alkanes with a boiling point of 130°C; (2) high density of 0.89 to 0.98 g/cm^3, relatively high asphaltene (5–18 percent) and sulfur (2–5 percent) contents, and few or no oxygenated compounds; and (3) high content of vanadyl porphyrins (600–3400 g/t) and vanadium (200–1400 g/t), with a V/(A+Rm) ratio of 1200–2500 g/t.

The fields of the early catagenetic subtype are concentrated at depths of 1.5–2.0 km in two types of basins: (a) those formed at the end of the Paleozoic Hercynian phase of folding, and (b) those

related to Cenozoic intermontane basins. This corresponds to the ascertained patterns of distribution (Raaben, 1978) of shallow pools. Such metalliferous deposits have been found and/or predicted in the Volga-Urals, Cis-Appalachian, Surkhan-Vakhsh, Santa Maria, and Adriatic Basins.

Examples of the early catagenetic subtype are the deposits of high-vanadium, high-cyclic heavy oils of the Volga-Urals area, the source of which may have been the Upper Frasnian-Tournaisian metalliferous domanikites of the Kama-Kinel' system of uncompensated depressions. In the zones of these depressions in which the extent of transformation of organic matter is lowest (stage of catagenesis of PK_3-MK_1), maximum concentrations of V (600–1400 g/t) and Ni have been found in the petroleum of the Zimnitskoye, Kondakovskoye, and Stepnoye Fields) (Figures 3.4–3.6).

The supergene-residual subtype

The supergene-residual subtype of metalliferous deposits of heavy oils and bitumens is related to concentrations of V, Ni, Re, Mo, and other rare and disseminated elements in residual accumulations of asphalt-resin substances during supergene alteration of originally metalliferous, relatively light petroleum. This is confirmed by the fact that the concentration of the individual elements per unit of asphalt-resin substance of both light and heavy oils and bitumens remains constant, on the whole, for a certain basin and genetic type of petroleum. In particular, our calculations show that for originally vanadiferous petroleum and bitumen, the amount of vanadium in the asphalt-resin substances averages 340 g/t in the Volga-Urals Province; 360 g/t in the Timan-Pechora Province; 365 g/t in the Surkhan-Vakhsh Province; 255 g/t in the Middle Ob' Province; and 330 g/t for the maltha-high resin petroleum of the Western Canada asphalt belt (oil sands).

On the basis of the analytical relationships, it has been found that for deposits of this type, maximum concentrations of V do not exceed 120–180 g/t in heavy oils, 130–300 g/t in maltha-asphalt, and 300–400 g/t in asphalt. Maximum concentrations of Ni are not more than 65–85 g/t in heavy oil, 70–140 g/t in maltha-asphalt, and 140–230 g/t in asphalt. Despite the relatively low concentrations of V and Ni, individual fields with large reserves of heavy oil and bitumens are of interest in connection with by-product extraction of metals including several fields in the Volga-Urals, Timan-Pechora, Middle Ob', Lena-Anabar, Western Canada, Persian Gulf, and other provinces).

The fractional subtype

The fractional subtype is related to the accumulation of ore concentrations (V, Ni, Mo, and Re, and, less often, Ag, Au, As, Sb, Cd, and others) during deposition of the originally metalliferous high molecular weight compounds in heavy oils during the formation of vein asphalt bitumens. The conditions most favorable for finding them are: (1) suture faults, overthrust zones, and tension fractures branching from regional faults; (2) faults with open fractures, arising during the growth of structures; and (3) the presence in the section of deposits of metalliferous immature petroleum, that is, heavy crude oil at an early stage of generation, and residual heavy crude-maltha.

In some deposits of vein asphaltite (Volga-Urals, Adriatic, and other provinces), the content of V reaches 1200–6000 g/t, Ni, 500–1200 g/t, and Mo, 20–50 g/t, with a high percentage of these metals in the asphalt-resin substances, in which V/(A+R) > 2500 g/t and Ni/(A+R) > 500 g/t.

TABLE 3.13

Genetic classification of metalliferous deposits of heavy oil and bitumen

Genetic type	Subtype	Ore-bearing naphthides	Ore elements (C_c in %)	By-product elements	Geochemical indicators	Districts of occurrence
Organophilic	Early catagenetic	Heavy high-cycle petroleum (immature petroleum and maltha)	V (0.2–1.4) · 10^{-1} Ni (0.1–0.2) · 10^{-1} Mo (1–15) · 10^{-4} Re (0.2) · 10^{-4}	Zn, Pb, Co Cr, Cu, Pb Au, Ag, As Ga, Se, Sb	V/Ni = 1–4.5 (V)/(A + R) = (1.2–2.5) · 10^{-1}% V/S = (5–35) · 10^{-3} VO – P = 600–3400 g/t	Melekess, South Tatar, Upper Kama, Surkhan-Vakhsh, South Adriatic, Los Angeles, Santa Maria
	Supergene residual	Heavy, oxidized high-sulfur petroleum, maltha, asphalt, asphaltite	Heavy oil V (0.12–0.18) · 10^{-1} Ni (0.08–0.1) · 10^{-1} Re (0.1) · 10^{-4} Bitumens V (0.2–0.4) · 10^{-1} Ni (0.1–0.2) · 10^{-1} Re (0.8) · 10^{-4}	Mo, Co, Cr La, Ce, As Sb, Ag, Au Zn, Se, Sc	V/Ni = 1.5–2.5 (V)/(A+R)<5·10^{-2}% (Ni)/(A+R)<2.5·10^{-2}% (V)/(S) = (1.2–5)·10^{-3}	Western Canada oil sands, Timan-Pechora, (Izhma-Pechora, Varandey-Adz'va), Lena-Anabar, Middle Ob', Persian Gulf
	Fractionated	Vein asphaltite, asphaltenite	V (1.2–6.0) · 10^{-1} Ni (0.5–1.2) · 10^{-1} Mo (2–5) · 10^{-3} Re	Ag, Au, Sb, As, Co, Cr, Ce, La	(V)/(A+R)>2.5·10^{-1}% (Ni)/(A+R)>0.5·10^{-1}% (V)/(S) > 4 · 10^{-2}	Middle Volga, South Adriatic, Ouachita

Table 3.13 cont'd ...

Genetic type	Subtype	Ore-bearing naphthides	Ore elements (C_c in %)	By-product elements	Geochemical indicators	Districts of occurrence
Secondarily concentrated	Barrier	Heavy biodegraded oil, maltha, oxyasphalt-ozokerite	Heavy oil-maltha V (0.2–1.2) · 10^{-1} Ni (0.05–0.15) · 10^{-1} Mo (8–10) · 10^{-4} V (0.01–0.5) Mo (0.01–0.7) Se (0.05–0.2) Ge (0.1–0.15) · 10^{-1}	As, Cu, Co, Pb, Sb, Ga, Ag, Zn, Cr, Re	V/Ni = 4–12 (V)/(A+R)>0.6·10^{-1}%	Orinoco, Maracaibo, Barinas-Apure, North Caspian, Grants Mineral Belt
	Hydrothermal metasomatic	Kerite, anthraxolite, petroleum coke	V (0.1–6.2) Mo (0.1–1.0) As, Au, Ni, Sc, U, Hg, Sb	Cu, Pb, Zn, Sb, Ag, Tl, Re, Se	–	Folded regions: Ural, Andean, Alpine, Volga-Ural, Timan-Timan-Pechora, Lena-Tungusska
	Emanational	Petroleum	Hg (0.1–2.9) · 10^{-3} Sb (0.1–4.0) · 10^{-3} Cd	–	–	California basins, Cis-Carpathian, South Mangyshlak

FIGURE 3.4

Metalliferous petroleum of the Early Carboniferous producing complex in the Volga-Urals complex, with schematic representation of zones of generation and accumulation [Compiler: I.S. Goldberg]

1 – Boundaries of the Kama-Kinel system of depressions
   1. Shalim
   2. Sarapulka
   3. Lower Kama
   4. Aktanysh-Chisma
   5. Mozhga
   6. Ust-Cheremshan
   7. Mukhanovo-Yegokhovsk
2 – Zone of bituminous limestones, marls, and shales of the Domanik facies (D_3–C_1t)
3 – Contours of the carbonaceous Devonian sequences
4 – Boundaries of depressions
5 – Contours of equal concentrations of vanadium in crude oils
6 – Zones of generation of metalliferous Early Carboniferous petroleum
7 – Zones of accumulation of metalliferous petroleum
8 – Presumed direction of migration of petroleum
9 – Boundaries of occurrence of vanadiferous petroleum
10 – Metalliferous bitumen related to Early Carboniferous petroleum
11 – Order of concentration of disseminated elements in shales
12 – Order of concentration of disseminated elements in heavy oil and bitumen

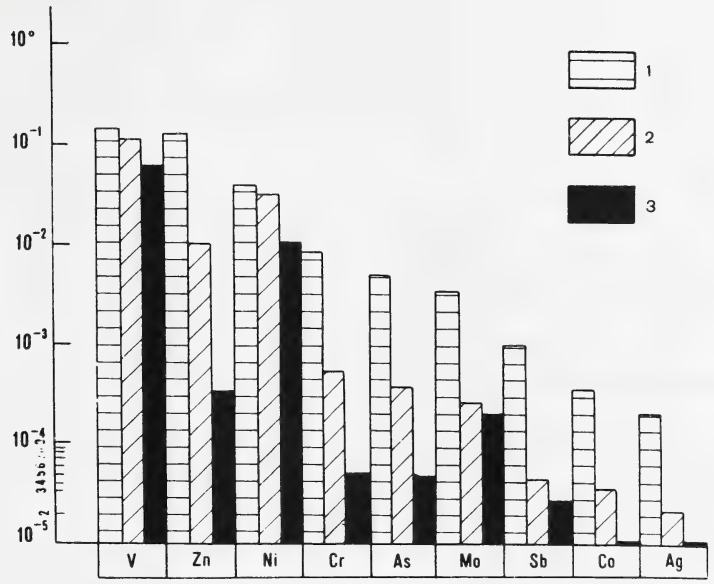


FIGURE 3.5
Correlation of metal concentration in Upper Devonian domanikite, chloroform-extractable bitumen, and primary heavy oil of Lower Carboniferous age in the Ust-Cheremshan depression

1 – Oil shale
2 – Chloroform-extractable bitumen
3 – Heavy oil

Secondarily Concentrated Type of Metalliferous Deposit

The secondarily concentrated genetic type of deposit is characterized by a considerably greater diversity of ore elements than in the case of the organophilic type; in addition to V and Ni, economic concentrations of Mo, U, Se, Hg, Ge, Sc, and others occur.

The barrier subtype

The barrier subtype is formed as a result of secondary enrichment of heavy oils and bitumens in metals (V, Mo, U, and Ge) due to their sorption by the asphalt-resin components from surface waters and slightly mineralized ground waters in whose catchment areas the rocks contain these elements. This is particularly true of ultramafic and mafic rocks for V, Ni, and Cr, and coal-bearing rocks for Ge, U, and so on.

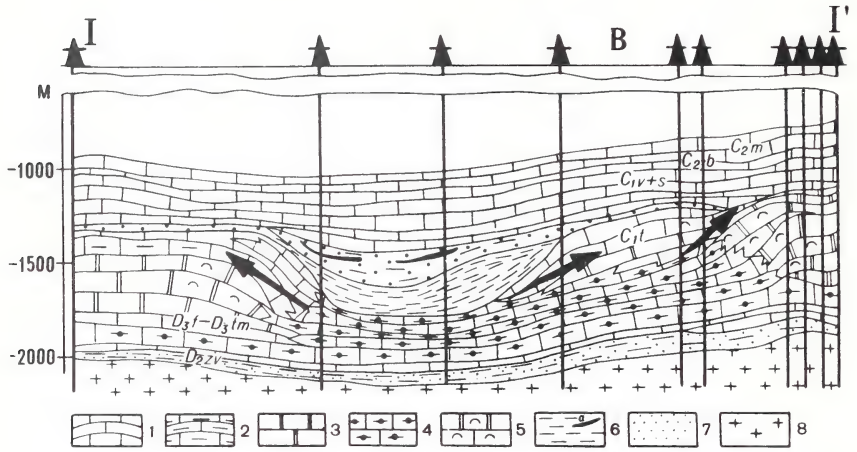


FIGURE 3.6

Cross section showing geologic units of the Ust-Cheremshan foredeep along the Mordovino-Nurlaty line [Source: M.F. Mirchink, Kinel'skaya Sistema Progibov]

1 – Limestone
2 – Shaly limestone
3 – Dolomite
4 – Bituminous shaly limestone and shale
5 – Reef limestone
6 – Coal-bearing shale and coal
7 – Sandstone
8 – Granite gneiss

As asphalt-resin and, probably, sulfur compounds play the main part in the accumulation of vanadium in petroleum, only petroleum that is oxidized and contains secondary sulfur has this capacity. Certain boundary values of the concentration of asphalt-resin substances and sulfur have been observed, below which there is no secondary introduction of vanadium into petroleum (Goldberg, Kaplan, and Ponomarev, 1986). That same feature has been observed for uranium, which can be extracted from water only by oxidized heavy oils. Probably oxidation processes, accompanied by secondary introduction of sulfur into petroleum in the reservoir, precede its substantial enrichment in these metals.

The vanadiferous heavy and extra-heavy oil fields of the Eastern Venezuela and Maracaibo Basins and the Big Horn Basin heavy oils are of this subtype. This is indicated by the relationships between [V] and [A+Rm], [Ni], [S], and density that we calculated for secondarily-enriched vanadiferous petroleum and bitumens, on the basis of analytical data.

Eastern Venezuela Basin:

(1) $[V] = 302\,\rho^{13.2}$

(2) $[V] = 51.3 \cdot 10^{9 \cdot 10 - 3[Ni]}$

Maracaibo basin:

(3) $[V] = 481\,\rho^{10}$

(4) $[V] = 11.75\,[Ni]^{0.93}$

where ρ is the density of the petroleum in g/cm^3.

The fairly high original content of vanadium, as well as of vanadyl porphyrins, in the petroleum of the Maracaibo basin ($[V] = 727.3\,\rho - 603.6$) probably is related to the presence of highly carbonaceous source rocks of the domanikite type (La Luna Formation) in the section.

On the basis of a genetic model of the formation of this subtype of metalliferous deposits of heavy oil and bitumens, the conditions most favorable for their finding are: (1) zones in the marginal parts of oil and gas basins, where there are fresh or only slightly mineralized waters related to exposures of the rocks of permeable complexes whose catchment basins are massifs containing ultramafic and mafic rocks; (2) areas where fresh or only slightly mineralized infiltrating waters occur in the interior parts of basins, under conditions of poor vertical insulation due to absence of a regional caprock or presence of such features as erosional valleys, which result in good vertical communication; (3) the presence of germanium-bearing carbonaceous formations in the stratigraphic section of the producing deposits; and (4) large hiatuses and unconformities at the boundary of the oil and gas-bearing complexes, accompanied by deep erosion, the occurrence of paleokarst or leached lenses, or the absence or erosion of a regional caprock.

Related to the processes of endogene introduction of elements (V, Mo, U, Hg, Sb, Sc, and Au) are the formation of secondary ore concentrations in deposits of solid bitumens in folded regions, and the introduction of Hg, Sb, and Cd into petroleum by gaseous emanations in zones of deep faults within oil and gas basins. This type of deposit has been studied very, very little, except in some basins abroad. However, according to available data we can point out one important trend: the metallogenic specialization of natural bitumens developed in mobile belts is governed by the ore potential of the latter. Thus, highly vanadiferous bitumens are related to the Ural vanadium province (gabbro-pyroxenite-peridotite belt), the ore belt of the Andes, and the Appalachian belt. The deposits of vanadiferous asphaltite (possibly kerite and anthraxolite) in the Andean folded system in Peru (Minas Ragra) and Colombia (Los Costanos, Milin Largo) have been studied the most. The Minas Ragra deposit was worked for vanadium from 1907 to 1955; in the 1930s, it yielded about 80 percent of the world's vanadium production. The vanadium content in the ore mass is 6.2 percent, in the ash up to 36.4 percent. The main source of the vanadium was natronite (VS_4).

In the bitumen of the Urals, from albertite to lower anthraxolite in the Velikhovskoye, Akbulak, Troitskoye, and other accumulations, the vanadium content reaches 1230 g/t, and a broad spectrum of other elements, such as Ni, Mo, Pb, Ag, Cr, and Zn, is present. Anthraxolite containing, in the ash, 9–60% V_2O_5 and 2–3% NiO, has been found on Novaya Zemlya, Spatial associations of

metamorphosed vein bitumens (kerite and anthraxolite) with deposits and shows of mercury, and, often, antimony, are observed in the Northeast USSR at Koryak-Kamchatka, in the Verkhoyansk-Chukotka folded region, in the folded zones of the Greater Caucasus, and elsewhere. It is believed that these bitumens were transformed in a very high temperature stage preceding deposition of the ores, or else their formation was related to pyrolysis of host rocks rich in organic matter.

The manifold conditions and forms of concentration of various metals in the bitumens of mobile belts require that special investigations be carried out.

4

DISTRIBUTION PATTERNS OF METALLIFEROUS HEAVY OIL AND NATURAL BITUMEN AND PREDICTION OF ZONES OF OCCURRENCE

The environment of formation and patterns of distribution of metalliferous deposits of heavy oils and bitumens in the oil and gas basins in various parts of the world were established on the basis of naphthometallogenetic regionalization. Genetic models were developed for those deposits and analytical and calculated data were obtained on the concentrations of the metals (V and Ni), making use of the information available to us.

Table 4.1 gives composite data on the metal content of petroleum and bitumens from the various types of naphthometallogenic provinces and the levels of concentration of rare and disseminated elements in them which may be of economic interest. Table 4.1 shows that heavy oils and bitumens enriched in V, Ni, and other rare and disseminated elements are related mainly to vanadium and nickel-vanadium provinces, among which the Eastern Venezuela, Maracaibo, Western Canada, Volga-Urals, and others stand out in resources of petroleum and bitumen which contain vanadium.

4.1 THE FORMER SOVIET UNION

Volga-Urals Province

The Volga-Urals province contains the main resources of vanadium contained in petroleum and bitumen in the former Soviet Union. Within this province, several districts with accumulations of vanadiferous petroleum and bitumen are distinguished. These are confined to the Melekess, Abdulinsk, and Upper Kama intra-cratonic basins and the adjacent slopes of large uplifts, such as the South Tatar and Zhiguli arches and the Birsk saddle (Figure 4.1). In addition, zones of occurrence of vanadiferous petroleum and bitumens often are attributed to the Kama-Kinel' system of uncompensated depressions: the Ust'-Cheremshan depression in the Melekess Basin, the Sarapul'Upper Kama Basin, and the Aktanysh-Chishma-Birsk saddle (Figure 3.4).

In order to study the patterns of accumulation of rare and disseminated elements, in particular vanadium, in the petroleum and bitumens of the Volga-Urals province, we correlated the vanadium concentration with the physico-chemical parameters of the petroleum (Figure 4.2) (Goldberg, Kaplan, and Ponomarev, 1986).

Figure 4.2 shows the relationship between V and the content of asphalt-resin substances in petroleum and bitumens, with three zones indicated, each characterized by different patterns of vanadium accumulation. In vanadium concentration intervals of 10 to 120 g/t (zone I), the concentration of V increases in proportion to the content of asphalt-resin substances. This relationship is described by the formula:

$$(1) \quad [V] = 3.58\,[A + R] - 2.51$$

where [V] is the vanadium content of the petroleum or bitumen, in g/t, and [A+R] is the sum of asphaltenes and resins, in percent.

Most petroleum in the province belongs to zone I, except for the Melekess Basin, Abdulinsk depression, and the west flank and central part of the South Tatar arch. The observed correlation between [V] and [A+R] is indicated regardless of the geologic age of the petroleum.

In vanadium concentration interval of 120 to 240 g/t (zone II), there is no functional relationship between vanadium and asphalt-resin substances. The petroleum of the Devonian and Lower

Carboniferous pools in the Radayevskoye, Sultangulovskoye, and other fields of the Abdulinsk depression and the Lower Carboniferous and Upper Permian petroleum in the Mordovo-Karmal'skoye, Shugurovskoye, and other fields of the South Tatar arch, belong to this zone.

For vanadium concentrations of more than 250 g/t in petroleum and bitumen (zone III), a linear relationship between [V] and [A+R] is again observed, characterized by different relationships for the Upper Permian and Lower Carboniferous deposits of the west flank of the South Tatar arch and the Melekess basin:

Upper Permian:

(2) $[V] = 12.31 [A + R] - 100$

Lower Carboniferous:

(3) $[V] = 12.73 [A + R] + 178.49$

Ascertaining the dependence on [V]/[A+R] on the amount of vanadium per unit of asphalt-resin substances in petroleum and bitumen is of special interest (Figure 4.2). The petroleum of different horizons with vanadium concentrations up to 120 g/t has constant values of [V]/[A+R], equalling 340 g/t on average, which indicates that the petroleum is of the same type. As the concentration of vanadium in petroleum increases from 120 to 240 (zone II), the vanadium content per unit of asphalt-resin substances increases in proportion, from 340 to 1160 g/t. The relationship between [V] and [V]/[A+R] is expressed by the formula

(4) $[V] = 0.512 [V]/[A + R] + 70$

For the regions of maximum accumulation of vanadium in petroleum and bitumen, the Melekess basin and west flank of the South Tatar arch, two relationships between [V] and [V]/[A+R] have been found, with average values of 1000 g/t (Upper Permian heavy oil and bitumen) and 1580 g/t (Lower Carboniferous heavy oils and malthas):

(5) $[V] = 1000 [A + R]$

(6) $[V] = 1580 [A + R]$

In addition, the vanadium concentration in asphalt-resin substances of some Lower Carboniferous heavy oil is higher than the average, reaching 2220 g/t in the Zimnitskoye Field and 2750 g/t in the Nurlaty Field.

On the basis of the experimental data that we have presented, the following features of accumulation of vanadium in petroleum and bitumen in the Volga-Urals province have been found.

In Zone I, the correlation between vanadium and asphalt-resin substances for various types of petroleum, in the face of constant values of [V]/[A+R], indicates primary accumulation of vanadium inherited from the original organic matter. In originally vanadium-bearing petroleum, a linear relationship has been established between the concentrations of vanadyl porphyrins and asphalt-resin substances, expressed by the formula

TABLE 4.1
Metallogenic types of world oil and gas basins, based on distribution of rare and disseminated elements in the petroleum and natural bitumen

Oil and gas basin	Country	Age of oil-bearing (P) and bitumen-bearing (B) deposits	Definitive trace element (based on absolute concentration)	Trace element associations (based on maximum concentration coefficients)		Established above-clarke concentrations of trace elements (g/t)	
				Main	Secondary	Petroleum	Natural bitumens
I. Vanadium and nickel-vanadium Subtype Ia — (Re)-V-Ni-Mo [Mo-V-Ni]							
Volga-Urals	Russia	D_3, C_1, C_2 (P) P_2 (B)	V V, Ni	(Re)-V-Ni-Mo V-Mo-Ni	Au-As Sb-Zn	Heavy oil V-200–1460; Ni-100–195; Mo-2.2–15	Maltha, asphalt V-230–600; Ni-100–190; As-up to 60; Au-up to 0.1 Vein asphaltite V-2350–4800; Ni-520–708; Mo-22
Surkhan-Vakhsh	Tadzhikistan, Uzbekistan	(P)	V, Ni	V-Mo-Ni	–	Heavy oil V-230–1300 Ni-100–195 Mo-3.2–15	– –
Maracaibo	Venezuela	$P_2 - P_3$, N (P)	V, V, Ni	V-Mo-Ni	Se-Sb-As	Heavy oil V-130-1100 Ni-up to 150 Mo-up to 8	–
Eastern Venezuela (Orinoco belt)		K, P_3, N (P, B)	V, Ni	Mo-V-Ni	Se-As-Sb	Heavy oil-maltha V-180–490 Ni-up to 100	
Western Canada (oil sand)	Canada	K_1 (B, P)	V, Ni	Mo-V-Ni	Se-As-Sb	Maltha-heavy oil V-145–200 Mo-5–7.5	

Table 4.1 cont'd ...

Oil and gas basin	Country	Age of oil-bearing (P) and bitumen-bearing (B) deposits	Definitive trace element (based on absolute concentration)	Trace element associations (based on maximum concentration coefficients)		Established above-clarke concentrations of trace elements (g/t)	
				Main	Secondary	Petroleum	Natural bitumens
I. Vanadium and nickel-vanadium							
Subtype Ia — (Re)-V-Ni-Mo [Mo-V-Ni]							
Adriatic	Italy	K, P_2 (P) T, K, P_2, (B)	V, Ni	Mo-V-Ni	–	Heavy oil Mo-19.5	Maltha, asphalt V-190–250 Ni-100–155 Mo-80–170
Albania	(P, B)	V, Ni	Mo-V-Ni	–	Heavy oil	Asphalt V-160–330	 V-430–520 Ni-100–160
Subtype Ib — V-Ni							
Timan-Pechora	Russia	C, P, T (P) D_3-C_1 (B)	V, Ni	V-Ni	As-Au (B)	Heavy oil V-300	Asphalt, asphaltite V-180–435 Ni-100–340 As-up to 25 Sc (kerite)
North Caspian	Kazakhstan	C, P_1, T J_2, K_1 (P)	V, Ni	V-Ni	Au-As (B) Hg-Sb (P)	Heavy oil Heavy oil V-100–215	Maltha Asphalt As-20 Au-0.07 Ge (asphaltite)
Mesopotamia	Saudi Arabia	J_3, K (P)	V	V-Ni	Ag-Cd	Heavy oil Cd-2.3 Ag-0.4	–

Table 4.1 cont'd ...

Oil and gas basin	Country	Age of oil-bearing (P) and bitumen-bearing (B) deposits	Definitive trace element (based on absolute concentration)	Trace element associations (based on maximum concentration coefficients)		Established above-clarke concentrations of trace elements (g/t)	
				Main	Secondary	Petroleum	Natural bitumens
I. Vanadium and nickel-vanadium Subtype Ib — V-Ni							
Mesopotamia	Syria	T_3, K_2-N	V	V-Ni	–	Heavy oil V-130–520	–
II. Nickel and vanadium-nickel Subtype IIa — (Se)-Ni-V-Mo							
Los Angeles	U.S.A.	N_1–N_2 (P)	Ni, V	Se-Ni-V-Mo	–	Heavy oil Ni-up to 125	–
Great Valley	U.S.A.	N_1–N_2 (P)	Ni, V	Ni-V-Mo	Hg-Cd	Hg-up to 29 Cd-up to 3.9	–
Santa Maria		N_1–N_2 (P)	Ni, V	Se-Mo-Ni-V		Heavy oil Maltha V-up to 280 Mo-up to 4.6	– Ni-up to 174 Se-up to 1.4
Subtype IIb — Ni-Mo							
South Caspian	Azerbaydzhan Turkmenia	N_1–N_2	Ni	Ni-Mo	Au	Au-up to 0.009	–
Amu Dar'ya	Uzbekistan	J_2–K (P)	Ni	Ni-Mo	Au-Ag-As	Au-up to 0.003	–
South Mangyshlak	Kazakhstan	J_1–J_3 P–T (P)	Ni	Ni-Mo	–	–	–
Indolo-Kuban	Russia	P–N (P, B)	Ni, V	Se-Ni-V	Cd, Au, Sb	Heavy oil maltha Cd-0.7-8 Sb-up to 6.5 Ni-up to 105	– Au-up to 0.05 Se-up to 2

Table 4.1 cont'd ...

Oil and gas basin	Country	Age of oil-bearing (P) and bitumen-bearing (B) deposits	Definitive trace element (based on absolute concentration)	Trace element associations (based on maximum concentration coefficients)		Established above-clarke concentrations of trace elements (g/t)	
				Main	Secondary	Petroleum	Natural bitumens
Subtype IIc — (Se)-Ni-V Se-Ni							
Sahara-Libyan	Libya	K_2, $P_1 - P_2$ (P)	Ni	Se-Ni	Hg	Se-up to 1.8 Hg-up to 2.0	–
Cis-alpine	W. Germany	J_1, P_2 (P)	Ni	Ni-Se	Ag	Heavy oil Ag-up to 0.3	–
Subtype IId — Pb-Zn							
West Siberian (pri-Ural, Vasyugan OGD)	Russia	J_2, K_1 (P)	Ni, Zn	Pb-Zn	–	–	–
Baltic	Latvia, Russia (P)	$Є_2$, O_3	Ni, Zn	Pb-Zn	–	–	–
III. Zinc Subtype IIIa — Zn-Pb							
West Siberian (Yamal & Pur-Tazovsk OGD)	Russia	K_1–K_2 (P)	Zn, Ni	Zn-Pb	–	–	–
Uinta-Piceance	U.S.A.	C_2–C_3, T (P)	Zn, Pb	Zn-Pb	–	–	–
Subtype IIIb — Zn-Pb-Cu							
Lena-Tungusska (Nepa-Botuobuya OGD)	Russia	V-$Є_1$ (P)	Zn	Zn-Pb-Cu	–	–	–
Lena-Vilyuy	Russia	P_2, T, J_1, J_3 (P)	Zn	Zn-Pb-Cu	–	–	–

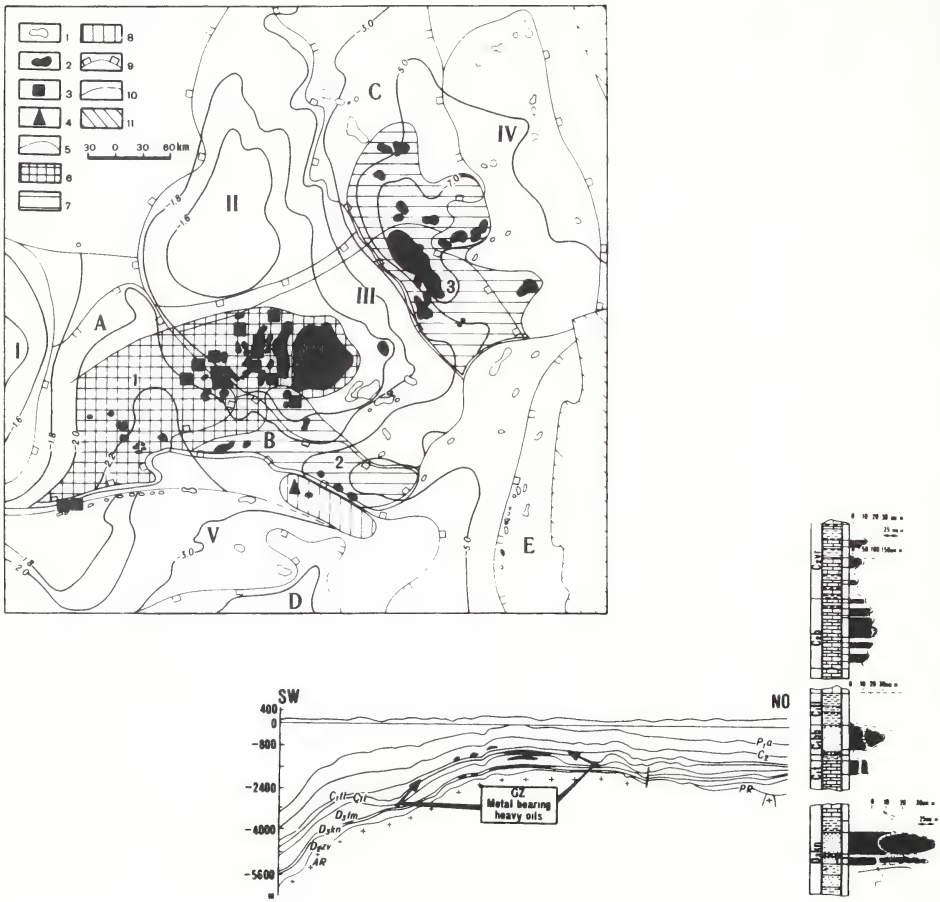


FIGURE 4.1

Map and generalized cross section of the metalliferous heavy oil and bitumen of the Volga-Urals province [Compiler: I.S. Goldberg]

1 – Oil fields
2 – Fields with metalliferous heavy oil
3 – Stratiform metalliferous bitumen deposits
4 – Vein metalliferous bitumen deposits
5 – Boundaries of zones of metalliferous heavy oil and bitumen
6 – Zones of vanadium-rich heavy oil
7 – Zones of vanadiferous heavy oil
8 – Zones of vanadium-rich bitumen vein deposits
9 – Boundaries of major structural elements
  I. Tokmovo
  II. North Tatar
  III. South Tatar
  IV. Perm-Bashkir
  V. Zhiguli-Orenburg arches
  A. Melekess
  B. Abdulinsk
  C. Upper Kama
  D. Buzuluk
  E. Belsk depression
10 – Deep faults
11 – Ural fold zone

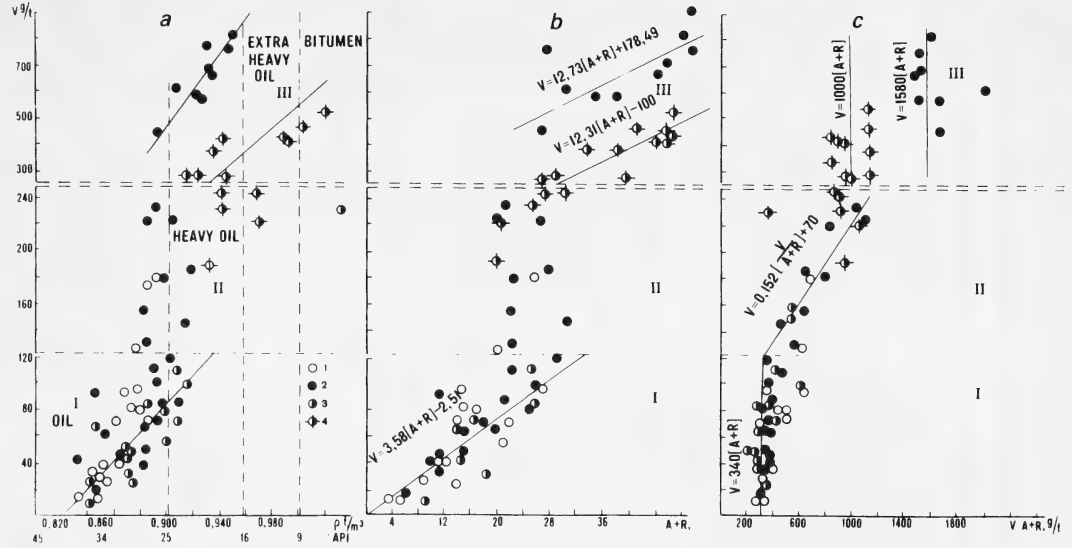


FIGURE 4.2

Dependence of vanadium concentration on density (a), resin- asphaltene content (b), and vanadium content of the resin-asphaltene component (c) of oil and bitumen in the Volga-Urals province

Petroliferous and bituminous horizons:

1. D_2–D_3
2. C_1
3. C_2–P_1
4. P_2

I – Zone of primary vanadium accumulation in originally light oil

II – Zone of secondary vanadium accumulation

III – Zone of primary vanadium accumulation in originally heavy, high-cyclic oil

(7) $[VO\text{-}p] = 2.1\,[A + R] - 2.1$

where [VO-p] is the concentration of vanadyl porphyrins in petroleum (mg/100 g).

In this type of petroleum and bitumen, the vanadium, vanadyl porphyrin, and nickel concentrations are proportional to the residual accumulation of asphalt-resin substances during supergene alteration of light oils. The extreme concentrations of vanadium in highly resinous petroleum are not more than 120–130 g/t, in maltha, 200–220 g/t, in asphalt, 260–280 g/t, and so on.

In secondarily vanadiferous petroleum of Zone II, the linear relationship between [V] and [A+R] is disrupted. It was established empirically that the minimum content of asphalt-resin substances for which petroleum can additionally accumulate vanadium is about 20 percent.

Zone III is similar to zone I of primary vanadium accumulation, but with a substantially higher content of vanadium (250–1465 g/t) in the heavy oil and bitumen and a special type of petroleum that is typical of so-called immature petroleum. Such metalliferous petroleum is formed from the organic matter of immature source domanikite for which the stage of catagenesis is not higher than MK_1. This takes place during early generation of originally heavy high-cyclic petroleum and liquid maltha enriched in high molecular weight and heteroatomic compounds of the early catagenic subtype. The zone of accumulation of such heavy oils and bitumens is confined to the Ust'-Cheremshan depression in the Melekess Basin, which is underlain by a sequence of Upper Frasnian-Tournaisian metalliferous domanikites that could have generated such petroleum. From the presumed zones of generation toward the South Tatar arch, there is a gradual decrease in vanadium concentration in the Lower Carboniferous deposits, from 1100–800 g/t in the Zimnitskoye, Kondakovskoye, Filippovskoye, and Pravda deposits to 600–400 g/t in the Il'movskoye, Yenoruskinskoye, Bureyka, and other deposits, to 300–200 g/t in the Yamashi, Novo-Yelkhovskoye, and Romashkino deposits (Figures 3.3, 4.3, 4.4). Concurrently, there is a decrease in the content of Co in the petroleum, probably also because of adsorption and chromatographic effects.

It is noteworthy that according to Belokon' (1987), the Kama-Kinel' system of depressions, underlain by Upper Devonian-Tournaisian domanikites, also tends to be the zone of maximum concentration of vanadyl porphyrins in petroleum. The VO-p content in the petroleum of the Bobriki horizon reaches a maximum value of 401.7 mg/100 g in the North Filippovskoye Field. Above and below the Bobriki horizon in the section, the concentration of vanadyl porphyrins in the petroleum decreases in the following order: $C_1bb > C_1t > C_2b > C_2vg > D_3fm > D_3kh > D_3p > D_2zhv$.

In addition to asphalt-resin substances, sulfur compounds play a definite part in the accumulation of vanadium in petroleum and bitumens. With vanadium concentrations of up to 120 g/t in petroleum, a proportional relationship is observed between [V] and [S] when the sulfur content is relatively higher in petroleum related to carbonate deposits such as the Middle Carboniferous-Lower Permian than in petroleum in clastic rocks, such as the Middle Devonian and Lower Carboniferous. The ratio [V]/[S] = (α) in this petroleum varies only slightly, from $1.5 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$. When the vanadium content increases from 120 to 300 g/t of petroleum (bitumen), the amount of vanadium per unit of sulfur concentration increases from $4 \cdot 10^{-3}$ to $10 \cdot 10^{-3}$. Secondary accumulation in petroleum and bitumens is expressed by the relationship

(8) $[V] = 26.2 \cdot 10^{-3}\alpha + 54$

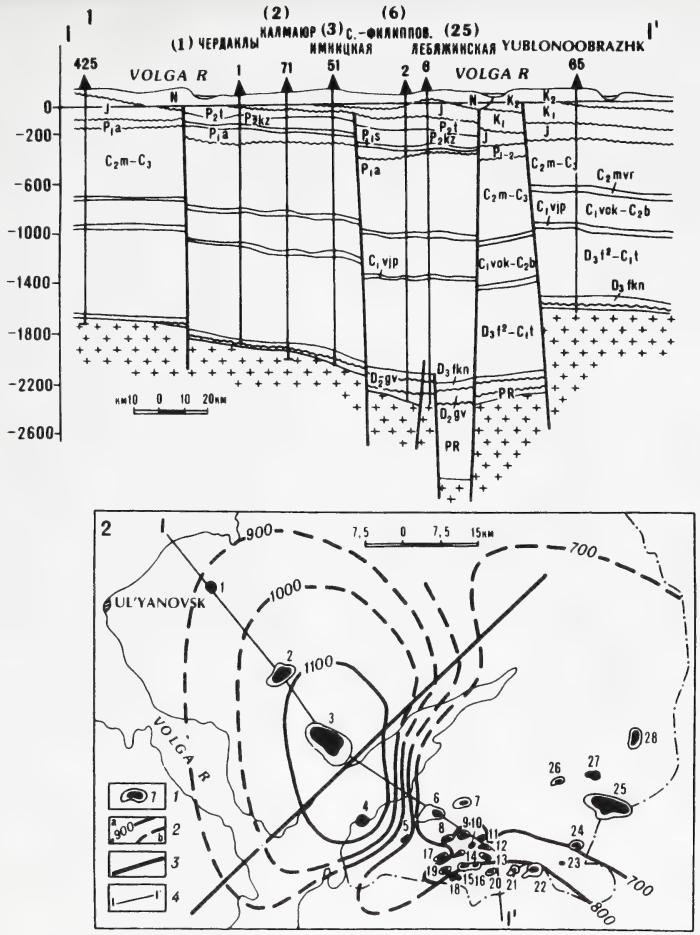


FIGURE 4.3

Map of oil fields in the Ul'yanovsk district containing vanadiferous petroleum in the Bobricki and Radayevsk horizons and cross section along I–I'

1 – Oil fields
1. Cherdakly
2. Kalmayur
3. Zimnitskoye
4. Kondakovskoye
5. Aleksandrovskoye
6. North Filippovskoye
7. Allagulovo
8. Pravda
9. Filippovskoye
10. Birlinskoye
11. East Birlinskoye
12. South Filippovskoye
13. East Filippovskoye
14. Vishenskoye
15. West Vishenskoye
16. East Vishenskoye
17. Bezymyannoye
18. Stepnoye
19. South Vishenskoye
20. West Raduzhnoye
21. Raduzhnoye
22. Pogranichnoye
23. Big Avral'
24. Nudryashovskoye
25. Labitovskoye
26. West Labitovskoye
27. North Labitovskoye
28. Novaya Bessovka

2 – Isopleths of vanadium concentration (g/t; a, established; b, presumed)

3 – Faults

4 – Line of cross section

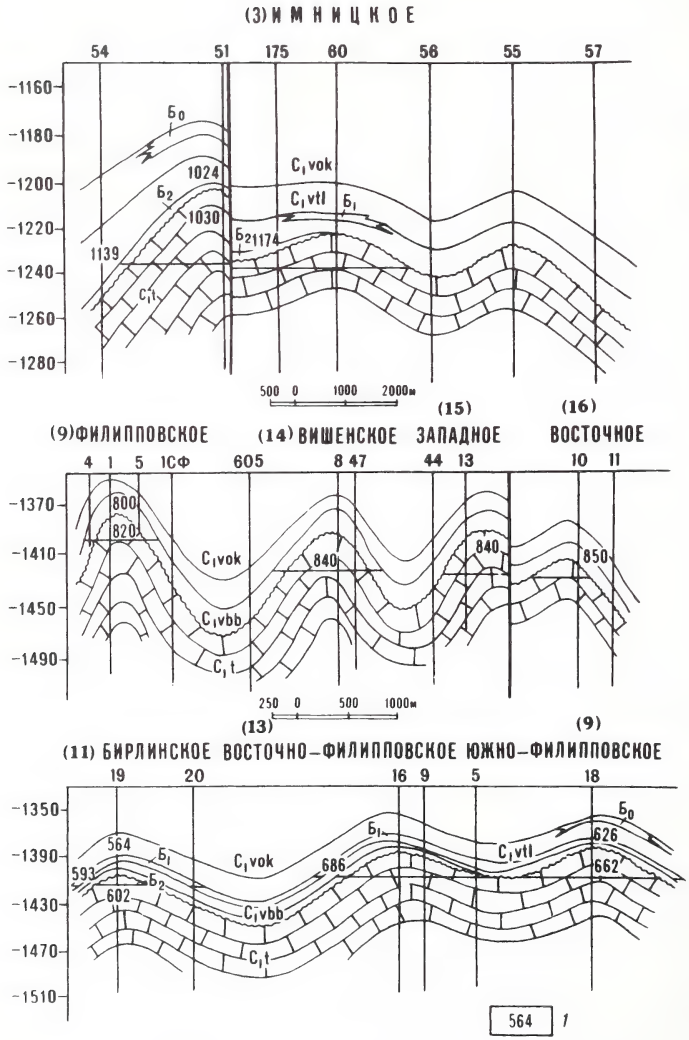


FIGURE 4.4

Cross sections through selected fields of the Ul'yanovsk district, showing vanadium concentration (g/t) in whole numbers in the pools (for oil field names, see Figure 4.3)

In highly vanadiferous heavy oils and bitumens (more than 300 g/t), V ranges from $8 \cdot 10^{-3}$ to $33 \cdot 10^{-3}$, reaching maximum values in the Lower Carboniferous petroleum of the Melekess basin. The relationship between [V] and α in this petroleum is expressed by the formula

(9) $[V] = 27.6 \cdot 10^3\alpha + 85$

The established relationships of vanadium accumulation make it possible to predict the concentration of this metal in petroleum and bitumens of various classes within certain zones of petroleum and bitumen accumulation (Table 4.2). For instance, we predicted the finding of the high-vanadium Zimnitskoye, Kondrakov, Filippovskoye, and East Birlinskoye Oil Fields in the Melekess basin and a number of fields on the west flank of the South Tatar arch (Nurlaty, Bureyka, Steynoozeroskoye, and Ul'yanovskoye). Testing of these fields showed that they have similar values (Table 4.3). This also pertains to other zones of petroleum and bitumen accumulation in the Volga-Urals province.

Ni, Mo, Re, Sr, Zn, As, Cr, Co, Cu, Sb, Tl, Pb, Ag, Au, Bi, Sn, and other rare elements have been found in association with vanadium in heavy oils and bitumens. The dominant group of elements is Ni, Sr, Zn, Mo, As, and Cr, with vanadium and nickel usually constituting at least 90 percent of the total rare and disseminated element concentration. On average, the nickel content of highly vanadiferous petroleum ranges from 50 to 185 g/t, with a V/Ni ratio of 2.5 to 7.7; the molybdenum content ranges from 0.5 to 15 g/t. As an example, Table 4.4 gives the elemental composition of heavy oils of the Nurlaty and Bureyka fields, determined by atomic emission spectrography with inductively-bound plasma (Institute of Nuclear Physics of the Academy of Sciences of Kazakhstan).

Despite the low concentration of most rare elements except vanadium and nickel in crude oils as a whole, when they are thoroughly refined the residual products, especially coke, are enriched in heavy metals. However, these metals (Mo, Cr, Re, and, less often, Au and others) can be considered useful by-products only in conjunction with vanadium and nickel.

The main economic reserves of vanadium mostly are concentrated in the Lower Carboniferous fields with heavy high-sulfur petroleum; Permian bitumen deposits of the Melekess Basin and west flank of the South Tatar Arch; Carboniferous heavy-oil fields of the Upper Kama Basin; and the vein asphaltites of the Malyy Kinel' zone (Figure 4.1).

The concentrations of vanadium and nickel in some heavy oil fields that have been tested in the South Tatar-Melekess district appear in Table 4.3.

In connection with estimating the reserves of vanadium in the petroleum of a number of deposits, such as Nurlaty and Bureyka, the distribution of vanadium by pool was studied in detail. The data obtained show that, on the whole, the concentration of vanadium in petroleum depends fairly clearly on the absolute depth of the producing formation, except for zones in which the reservoir formation has been replaced by compacted rocks, where the vanadium content drops off sharply (Figure 4.5). These patterns reflect variations in the physicochemical properties of petroleum (density, asphaltene, and resin content), the gas saturation from the crest to the limbs and noses of the pools, as well as the low-permeability zones. The contours of equal concentration of vanadium in petroleum of the producing formation more or less conform to the depth contours on the top of the formation, with minimum values of vanadium content in the higher parts of the pool. In slightly permeable zones of the formation, the reduction in vanadium content apparently is governed by the more difficult filtration of the petroleum (reduction in density and sifting out of metalliferous asphalt-resin components).

TABLE 4.2
Predicted concentrations of vanadium in heavy, highly-resinous petroleum and natural bitumen

Districts and regions of oil and bitumen accumulation	Age of producing complexes	Type of bitumen accumulation	Predicted concentration of V (g/t)				Fields with high-resin oils and bitumens
			Heavy oils	Maltha, high-resin oils	Asphalt	Asphaltite	
West flank of South Tatar arch	P_2	Stratiform	207–330	330–368	638–823	823–1070	Mordovo-Karmal'skoye, Gorskoye, Shugurovo
Melekess basin	C_1		222–625	625–1200			Yamashi, Novo-Yelkhovskoye, Aksubayevo-Moksha, Stepnoozerskoye, Bureyka Nurlaty, Filippovskoye, Kondakovskoye, Zimnitskoye
Zhiguli arch	C_3–P_1	Stratiform	–	123–212	212–265	265–338	Batrak, Syzran
Malyy Kinel'	P_2	Vein	–	–	–	2350–4510	Ivanovskoye, Sadki

TABLE 4.3
Vanadium and nickel concentration in heavy oil in selected fields of the Melekess Basin and South Tatar Arch

Field	V (g/t)			Ni (g/t)		Ratio V/Ni
	Producing horizon	range/average	No. of analyses	range/average	No. of analyses	
Zimnitskoye	C_2V^r	605	1			
	C_1V^{bb}	1024–1174/1127	4	152–185/168	2	6.7
Kondakov	C_1V^{bb}	1080–1465/1272	2			
Pravda	C_1V^{rd}	514–662/588	2			
	C_1^t	836–839/837	2	117	1	7.1
East Filippovskoye	C_1V^{rd}	674–698/686	2	111	1	6.1
Birlinskoye	C_1V^{bb}	516–593/564	3	86	1	6.5
	C_1^t	602	1	93	1	6.4
East Birlinskoye	C_1^t	540	1	130	1	4.1
North Labitovskoye	D_3f	330	1	65	1	5.1
West Labitovskoye	D_3fm	240	1	85		2.8
Nurlaty	C_2V^{r-b}	360–432/396	2			
	C_1V^{bb}	270–960/696	28	50–180/135	20	5.1
Bureyka	C_2V^{r-b}	295–401/400	3			
	C_1V^{bb}	324–554/424	33	35–74/55	21	7.7
Il'movskoye	C_1V^{bb}	420–760/560	7			
Ul'yanovskoye	C_1V^{bb}	350–480/381	7			
Ivashkino-Malaya	C_2V^r	274–277/275	2			
Sul'cha	C_1^t	595–611/603	2			
Steynoozerskoye	C_2V^r	204–262/233	2			
	C_1V^{bb}	445–585/515	3	95	1	5.4
Yenoruskinskoye	C_2V^{bb}	320	1			
	C_1V^{bb}	340–640/506	3	90–125/108	3	4.6
Aksubayev-Moksha	C_2V^{r-b}	190	1	65	1	2.9
	C_1V^{bb}	370–460/406	3	105–160/130	3	3.1
Yamashi	C_1V^{bb}	240–270/255	2	80	1	3.1
Arkhangel'skoye	C_1V^{tb}	240	1	80	1	3.0
Novo-Yelkhovskoye	C_1V^{bb}	300–358/329	2			
	C_1^t	240–251/245	2			
Romashkino pool 1	C_1V^{bb}	193–330/236	12	81	1	2.9
pools 5 & 8	C_1V^{bb}	220–220/206	3	70–95/80	1	2.5
pool 31	C_1V^{bb}	245	1	84	1	2.9

TABLE 4.4
Trace element composition of heavy oil from the Nurlaty and Bureyka fields (g/t)

Field	Nurlaty	Bureyka
Be	0.01	0.01
Na	85	285
Mg	22	50
Al	5.0	1.4
K	1.5	4.4
Ca	70	168
V	950	295
Cr	0.56	0.23
Mn	0.51	0.13
Fe	11.5	12.1
Ni	76	37
Cu	0.35	0.02
Zn	3.3	2.7
As	0.5	2.1
Sr	3.7	8.1
Mo	2.00	0.62
Cd	0.016	0.007
Sn	1.0	1.0
Sb	0.2	0.1
Tl	0.3	0.87
Pb	0.2	0.3
Bi	0.15	0.05
Ba	1.6	1.7

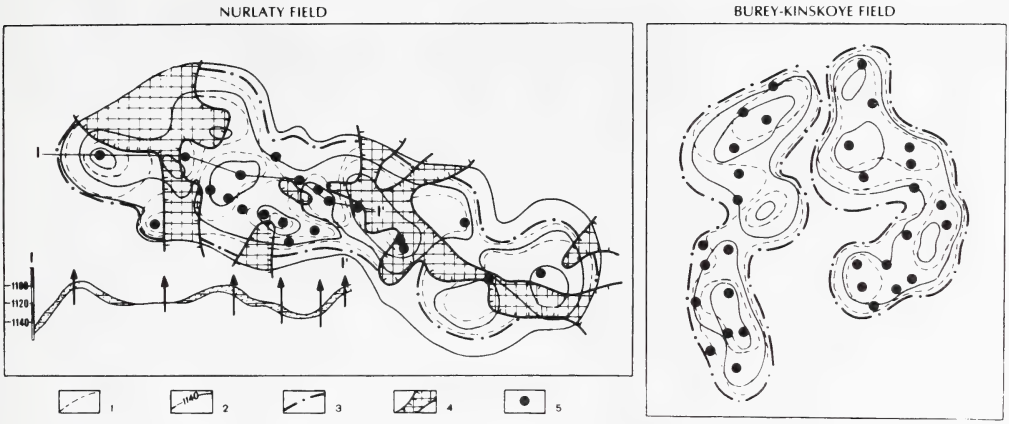


FIGURE 4.5

Distribution of vanadium in petroleum in the Early Carboniferous pools of the Nurlaty and Burey-Kinskoye Fields of the Volga-Urals province [Compiler: I.S. Goldberg]

1 – Isopleths of vanadium concentration
2 – Structure contours on top of the Bobriki horizon
3 – Edge of pool
4 – Zones where reservoir rocks are absent
5 – Wells tested for metals in the oil

In the Permian bitumen deposits of the Melekess basin and South Tatar arch, the vanadium and nickel concentrations are lower, on the whole, than in the heavy oils of the Carboniferous, in which they amount to 170 to 600 g/t and 40 to 70 g/t, respectively (Table 4.5). However, in connection with the substantial bitumen resources, the potential resources of vanadium in bitumen are much higher than those of vanadium in petroleum. There are plans to refine the Permian bitumens to obtain the liquid fuel and metalliferous coke components.

The vein asphalt deposits of the Malyy Kinel' zone in the Ivanovskoye, Kazanskoye, and Novoalekseyevskoye deposits can be considered to be economic vanadium ores. They have anomalously high concentrations of vanadium (2100–4860 g/t) and vanadyl porphyrins as high as 6400 g/t. The vanadium bound to porphyrins constitutes 24 percent. Besides vanadium, the asphaltite contains Ni, Fe, Mo, Cr, Zn, Se, Cu, Sb, and other elements, as well as 6.0–7.5 percent sulfur. The reserves of vanadium in asphaltite of the Ivanovskoye deposit alone are at least 21,000 tons, and of vanadyl porphyrins, 54,000 tons.

On the basis of conditions of concentration of metals (V, Ni, Mo, *etc.*), the asphaltite deposits belong to the fractional subtype. It is calculated that the source petroleum would have to have contained 750–950 g/t of vanadium, *i.e.*, the level of vanadium concentration typical of the heavy oils of the Melekess Basin, to produce such highly vanadiferous vein asphaltites. The metalliferous asphaltite deposits, Ivanovskoye and Kazanskoye, lie at depths of 400–450 m. At present, test work is being done on the production of asphaltite by water flooding.

TABLE 4.5

Estimated reserves of vanadium pentoxide from selected bitumen deposits of Permian age in the Volga-Urals area

Deposit	Age of producing horizon	Depth (m)	Bitumen reserves in-place/recoverable (10^3 t)	Average content of V_2O_5/V (g/t)	V_2O_5 reserves in-place/recoverable (10^3 t)
Gorskoye	$P_2KZ_1^2$	236–318	34,000/3400	822/462	28.0/2.8
Aksubayevo	P_2KZ_1	170–360	26,200/2620	729/409	19.0/1.9
Akan	P_2KZ_1	145–320	18,500/1850	740/415	13.7/1.3
Karasi	P_2KZ_1	207–311	39,000	685/385	26.7
Amal'chinskoye	P_2U_2	65–125	3569/357	427/240	1.5/0.15
	65–125	8954/895		3.8/0.38	
Mordovo-Karmal'skoye	P_2U_2	30–140	3772/377	414/232	0.7/0.07
Lower Karmalinskoye	P_2U_2	119–186	16,562/1656	498/280	8.2/0.82
North Karmalinskoye	P_2U_2	41–148	4009/401	578/325	2.3/0.23
South Ashal'-chinskoye	P_2U_2	60-130	6220/622	477/268	2.9/0.29
East Chumachka	P_2U_2	70–98	13,200/1320	409/230	5.4/0.5

Timan-Pechora Province

On the whole, the heavy oil and bitumens of the Timan-Pechora province have low contents of vanadium, nickel, and other rare elements, as is typical of metal deposits of the organophilic type related to oil and gas basins of the marginal systems of cratons. In this province, it is governed by the relatively high catagenesis of the organic matter in the petroleum source rocks, especially in the southern basins of the Cis-Ural depression and aulacogens. On the map of the zoning of the catagenesis of the organic matter at the base of the Lower Frasnian complex (Figure 4.6), it is seen that deposits of vanadiferous petroleum ($V \geq 80$–100 g/t) and bitumens are confined to relatively slightly heated zones, in which the transformation of organic matter did not exceed MK_2–MK_3, as in the Khoreyver Basin, Varandey-Adz'va Zone, and Central Pechora Uplift. Another factor controlling the distribution of petroleum and bitumens with high V and Ni contents is their relationship to certain petroleum source rocks. On the basis of the content of vanadium and nickel and their relationship to various parameters of the petroleum (density and content of asphalt-resins and sulfur) in the province, three geochemical types of petroleum are distinguished, having the following linear relationships (Figure 4.7):

(10) $[V] = 222 \cdot \rho - 175$

(11) $[V] = 567 \cdot \rho - 457$

(12) $[V] = 1822 \cdot \rho - 1470$

Relationship (10) is for the petroleum of the Ordovician-Lower Devonian oil and gas complex (Sed-Yaga, Khosoltinskoye, Nyadeyyu, and North Sarenbay Fields). This petroleum contains the minimum amount of vanadium in the asphalt-resin substances, averaging 150 g/t. The V/Ni ratio varies from 0.6 to 1.0. Calculations show that the petroleum of the OD1 complex, with a density of about 1.00 g/cm^3, cannot contain more than 50 g/t of vanadium. Considering that the organic matter in the rocks of this complex is sapropelic, such a low vanadium content in the petroleum can be explained by special conditions of generation of the hydrocarbons in regions of intensive catagenetic transformation of the organic matter in the source rocks, to MK_3–MK_4 or higher.

Relationship (11) is typical of most petroleum in the province, from light to heavy, related to producing complexes other than OD_1. Experimental and calculated values for the vanadium content in crude oils of different density are close and are governed by the following main concentration levels: 53–85 g/t in petroleum with a density of 0.900–0.955 g/cm^3 and 82–112 g/t, with a density of 0.955–1.00 g/cm^3. The V/Ni ratio varies from 1.4 to 2.0 percent and the sulfur content, 1.1 to 3.4 percent (Figure 4.7). Relative accumulation of V, Ni, Zn, Co, Cr, and Sr in heavy oils of this geochemical type occurred during supergene and paleo-supergene alteration of the original petroleum. This petroleum probably was formed in connection with the D_2–D_3f and D_2sm–C_1t petroleum-generating complexes in the stages of catagenesis to and including MK_2.

The third geochemical type of petroleum is described by relationship (12). Such petroleum has been found in Semilukian domanikoid deposits (South Taravey, Myadsey, and West Tebuk pools) and probably in secondary pools in higher in the section, such as the Sotchem'yu and Usino-Kushshor Fields.

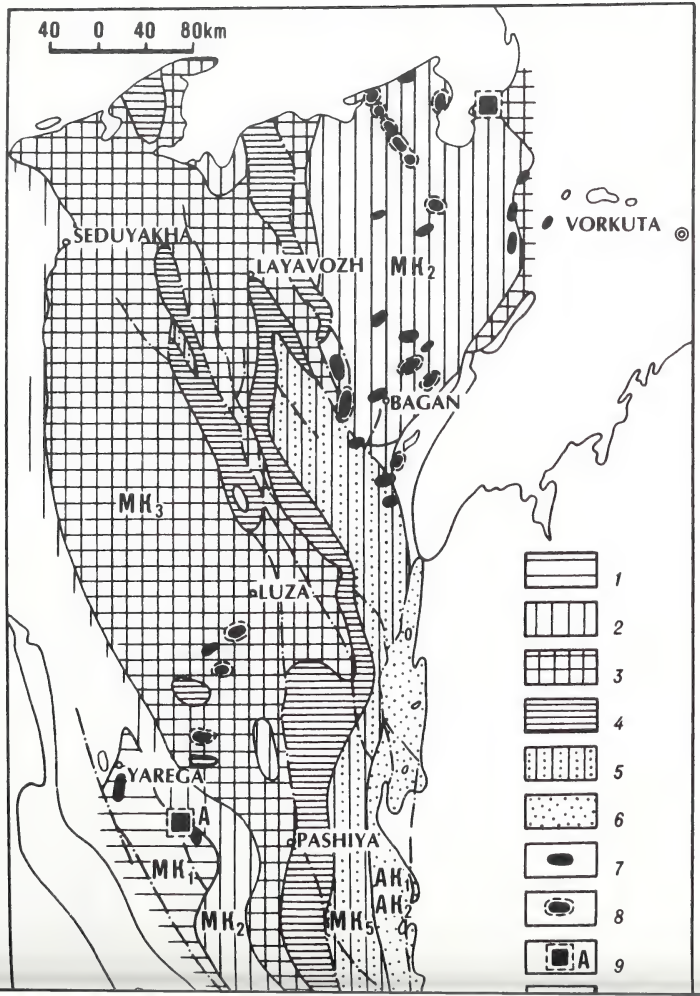
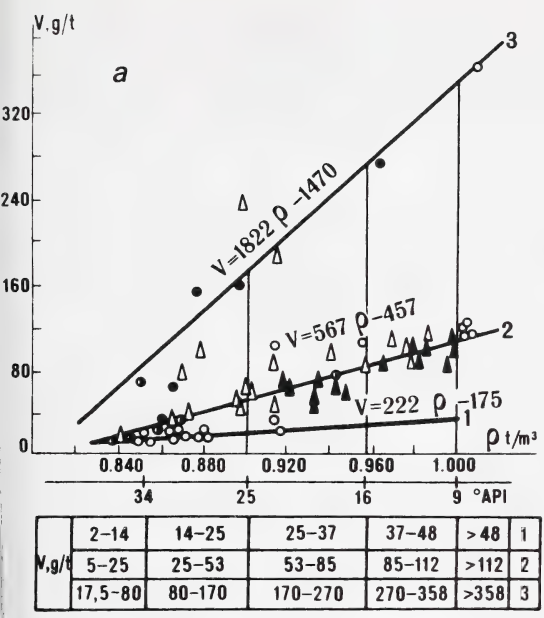


FIGURE 4.6

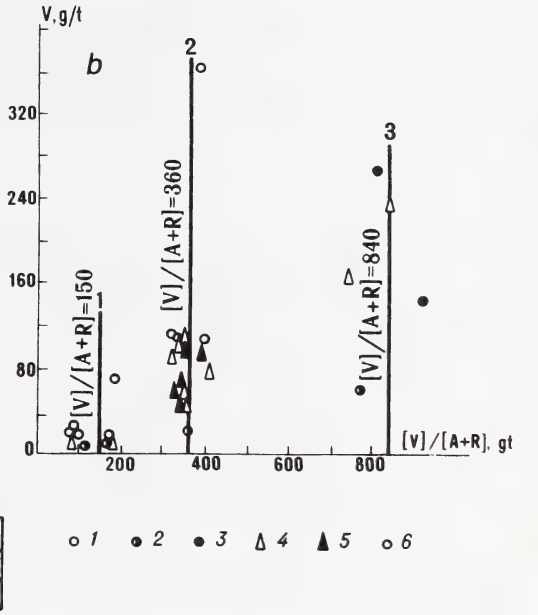
Map showing distribution of metalliferous petroleum and bitumen in the Timan-Pechora province and zones of catagenesis of organic matter to the base of the Frasnian oil and gas complex [after Danilevskiy and Sklyarova, 1986]

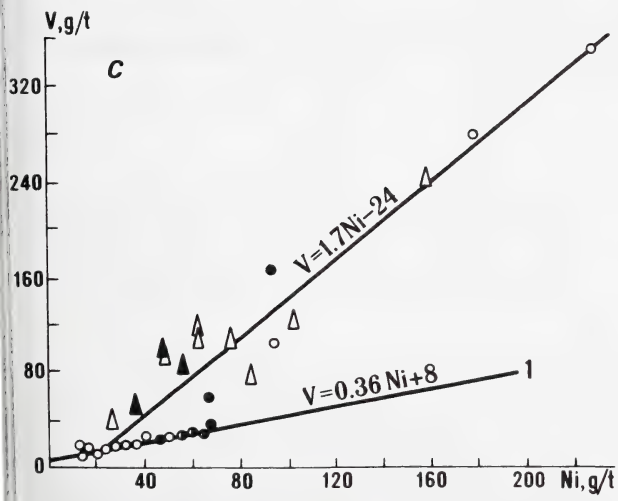
1 – 6 – Stages and substages of catagenesis
1 – MK_1
2 – MK_2
3 – MK_3
4 – MK_4
5 – MK_5
6 – AK_1–AK_2
7 – Fields tested for metal content
1. Yarega
2. Lower Omir
3. West Tebuk
4. Aress
5. Upper Kos'yu
6. Sotchem'yu
7. Vozey
8. Usa
9. Chedutay
10. Bagan
11. Salyukinskoye
12. Lizayu
13. Middle Makarikha
14. Salyukinskoye
15. Saydivey
16. Usa–Kushor
17. Varandey
18. Taravey
19. South Taravey
20. Nauk'skoye
21. Labagan
22. Toboy
23. Myadsey
24. Sed'yaginskoye
25. Nadeyyu
26. Khasirey
27. Cherepayu
28. Khoseltinskoye
29. North Sarembay
30. Ust'–Pyayyu
31. North Khosedayu
32. Pyzh'el'skoye
33. Subborskoye
34. South Syninskoye

8 – Vanadiferous oil fields ($V \geq 100$ g/t)
9 – Vanadiferous bitumen deposits of Izhem (A) and Talota (B) ($V \geq 100$ g/t)
10 – Principal faults



V,g/t	2–14	14–25	25–37	37–48	>48	1
	5–25	25–53	53–85	85–112	>112	2
	17,5–80	80–170	170–270	270–358	>358	3





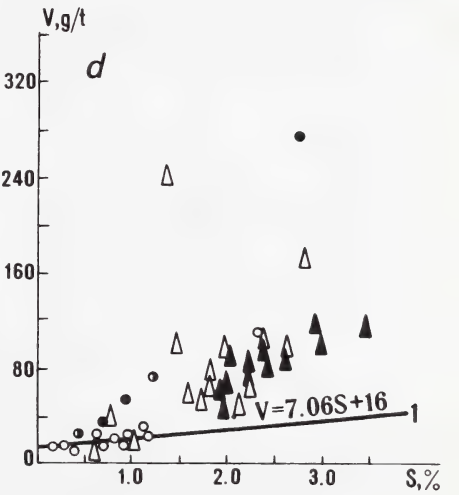


FIGURE 4.7

Vanadium concentration as a function of density of oil and bitumen (a), vanadium content of the resin-asphaltene component of oil and bitumen (b), nickel concentration (c), and sulfur concentration (d) in the Timan-Pechora province

1–5 – Oil-bearing horizons
1. S–D_1
2. D_2–D_3f_1
3. D_3f_2–C_1t
4. C_1–P_1
5. P_2–T

6 – Bitumen-bearing horizon: D_3–C_1

The heavy oils of these deposits contain very high concentrations of vanadium (150–274 g/t) and nickel (90–160 g/t), and also have a very high vanadium content in the asphalt-resin components (840 g/t). According to calculations, the extreme concentration of vanadium in extra-heavy oils may reach 360 g/t, and in solid bitumens, as much as 400–500 g/t. Heavy oils so rich in V and Ni probably were formed in the initial stages of generation (early catagenic subtype) in the Semilukian-Tournaisian complex.

These geochemical types of petroleum are also distinguished on the basis of vanadyl (VO) and nickel porphyrins, and their ratio, and correlate with the level of catagenic transformation of the organic matter. In petroleum in the final stages of catagenesis, nickel porphyrins predominate and vanadyl porphyrins are very low in amount or are entirely absent. In the petroleum in the initial stages of metamorphism, VO complexes of DPEP type predominate (Danilevskiy and Sklyarova, 1986).

These trends of accumulation of vanadium in the petroleum of the Timan-Pechora province make it possible to predict the possible levels of concentration of metal in petroleum on the basis of its genetic type, and also to distinguish targets with economic ore concentrations. Table 4.6 gives the results of testing for vanadium in a whole group of heavy oil deposits in the Khoreyver, Varandey-Adz'va, and Kolva zones of petroleum accumulation that were promising with respect to vanadium . The Permo-Carboniferous heavy-oil pool of the Usa Field and the Triassic heavy-oil pool of the North Sorokin-skoye Field have the largest vanadium reserves.

Metalliferous solid asphalt and asphaltite bitumens are confined mainly to the Izhma-Omri and Tolotinskoye-Nadeyyu zones in the province.

The vanadium content in the bitumens is 180 to 435 g/t and the nickel content 100 to 340 g/t, with a broad combination of other elements present (Table 4.7). The relatively high concentrations of Ag, Zn, and As in the bitumens are noteworthy.

North Caspian Province

Economic vanadium-bearing heavy oils in the North Caspian Province are found in the Buzachi oil district in the Karazhanbas, Kalamkas, North Buzachi, and Zhalgistyube Fields. The vanadium content in the crude oil ranges from 100 to 215 g/t, averaging 140 g/t; the nickel content is 27 to 50 g/t, averaging 37 g/t. Cr, Zn, Mo, Sb, As, and other rare and disseminated elements have been found in the crude, in addition to V and Ni (Table 4.8).

In refining the Karazhanbas heavy oil by thermal cracking, the vanadium content of the coke is 15.5 times higher than that of the oil and that of nickel 14 times higher, molybdenum 15 times, chromium 95 times, and so on (Table 4.9). This is governed by the fact that the heavy metals are confined to the high molecular weight compounds in the petroleum, mainly asphaltenes. According to analytical data, the vanadium content in the asphaltenes of the Karazhanbas oil is 1100–1200 g/t, and the nickel content is 520–540 g/t. The resins contain on the order of 300 g/t vanadium and 8–10 g/t nickel.

The reasons for the relatively high concentrations of vanadium in the heavy oils of the Buzachi peninsula compared to other districts of the province are not yet clear. Two possibilities can be suggested: (1) secondary enrichment of the petroleum in vanadium due to sorption from infiltrating, slightly mineralized waters of the Cenomanian deposits; and (2) The specific conditions of transformation of the original petroleum (Tengiz Carboniferous type of petroleum with a vanadium

TABLE 4.6
Results of determination of vanadium concentration in heavy oil from selected fields in the Timan-Pechora province

Field	Producing horizon	Interval (m)	Density ρ_4^{20} (g/cm^3)	Sulfur content, (%)	Vanadium content, (g/t)
Field	D_2	170–190	0.9413	1.15	78
Sotchem'yu	P	1846–1866	0.9002	1.31	240
Usa	P–C_3	1205	0.9861	1.78	113
Central Makharikha	P–C_3	1697–1743	0.9786	2.58	90
	S_2	3142–3172	0.9554	2.23	110
Salyukinskoye	C_2^2	1546–1600	0.912	1.95	85
Varandey	T_1	1346–1352	0.9978	2.09	80
Taravey	T_2–T_1	1176–1190	0.9865	2.31	97
South Taravey	P_2U	1325–1349	0.9323	1.95	43
	D_3f	2460–2484	0.9651	2.65	274
North Sorokinskoye	T_2	980–987	0.9981	2.84	110
	T_1	1105–1121	0.9892	2.75	100
	P_2U	1348–1360	0.9303	1.94	55
Naul'skoye	T_2	877–898	0.9809	2.55	83
Laboganskoye	P_2U	1235–1247	0.9646	2.96	86
Sed'yaga	P_2U	944–1020	0.9792	3.42	100
Usa–Kushshor	P_1–C_3	1758–1768	0.9189	2.72	176
Pyzh'elskoye	P_1	2400	0.9680	1.88	87
Subborskoye	P–C	2270–2473	0.9400	1.45	100

TABLE 4.7

Results of neutron-activation analysis of trace-element content of selected natural bitumen deposits in the Timan-Pechora province (g/t)

	Izhem/D_3^2-C_1V* asphalt**	Voyskoye/C_1V* vein asphaltite**	Talota/C_1V* asphalt**	Talota/C, V* thiokerite**
Sc	0.17	0.06	0.13	0.07
Cr	16.4	12.4	13.1	4.8
Co	1.6	1.2	0.8	1.0
Zn	112.0	74.0	≤ 74.0	
As	2.5	1.0	20.2–25.7	8.7
Se	0.6	0.6	0.6	
Rb	86.7	39.0	≤ 39.0	
Ag	4.0	2.1	1.0	
Cd	≤ 1.0	≤ 1.0	≤ 1.0	
Sb	1.4	0.4	0.4	0.2
La	1.8	3.4	0.6	0.5
Ce	5.8	5.7	0.5	
Sm	2.5	1.3	0.7	
Hf	1.10	2.23	1.30	0.16
Ta	0.24	0.22	0.20	0.006
Au	0.020	0.003	0.03	0.04
Tl	≤ 0.18	0.027	0.63	

* Deposit/age

** Class of bitumen

TABLE 4.8

Results of the determination, by atomic absorption spectroscopy with inductively-bound plasma, of the trace element content of petroleum from the Buzachi Fields [Source of analyses: Institute of Nuclear Physics of the Academy of Sciences of Kazakshtan] (g/t)

			Field		
	North Buzachi	Khalgiztyube	Kalamkas	Karazhanbas (well 206, 289–305 m)	Karazhanbas (well 106, 378–400 m)
Be	< 0.01	0.023	0.17	0.24	0.17
Al	1.8	2.8	1.1	2.5	8.3
V	130	135	100	142	145
Cr	–	0.22	0.35	0.47	0.6
Mn	0.06	0.45	–	–	–
Fe	4.5	90	4.0	4.6	7.8
Ni	37	37	27.3	39.4	37
Cu	1.5	1.1	–	0.48	0.17
Zn	< 0.17	< 2	0.71	2.57	0.33
As	1.0	6.0	0.82	4.54	4.5
Sr	0.12	0.63	0.21	0.18	0.27
Mo	0.31	0.34	0.26	0.038	0.036
Cd	< 0.01	< 0.01	0.026	0.038	0.036
Sn	< 1	< 0.5	< 0.5	< 0.5	< 0.5
Sb	0.07	0.2	0.2	0.27	0.29
Ba	0.36	0.72	0.24	0.37	0.29
Tl	< 0.1	< 0.2	0.5	< 0.5	< 0.5
Pb	0.43	2.1	0.34	0.55	0.86
Bi	< 0.07	< 0.1	0.13	0.2	0.11

TABLE 4.9
Results of the analysis of coke obtained from thermal cracking of petroleum from the Karazhanbas field

Element	Content (ppm)	Ratio of content of element in coke to that in petroleum
Aluminum	4500	
Scandium	0.9	
Vanadium	2200	15.5
Chromium	45	95
Manganese	50	
Iron	3800	
Cobalt	10	
Nickel	550	14
Zinc	30	11.6
Arsenic	15	3.3
Molybdenum	5	15
Antimony	4.9	18
Lanthanum	1.5	
Cerium	2.0	
Samarium	0.30	
Europium	0.05	
Dysprosium	0.20	
Rhenium	–	
Gold	0.045	
Thorium	0.46	

content of about 50 g/t) in the face of high gas saturation of the fluid, which could have led to deasphaltization of the petroleum in the pools and accumulation of metalliferous asphaltene components. In this respect it is noteworthy that the [V]/[A+R] ratio in the petroleum of the Buzachi Field is much higher, at levels of 550 to 1050 g/t, than the average value of that ratio for the petroleum of the province (230 g/t).

In other petroliferous zones of the North Caspian province (northern North Caspian, South Emba, Ural-Emba, and others), the heavy oils and bitumens, on the whole, have low concentrations of vanadium and other metals. The chances of finding economic vanadiferous oils probably are nil. In the kir deposits in these regions, which contain fairly large bitumen reserves, as at Mortuk and Akzhar, the concentration of vanadium is only 7–32 g/t, nickel, 23–28 g/t, cobalt, 10–14 g/t, and chromium, 37–52 g/t.

The reasons for the low metal content in the petroleum and bitumens probably lie in the specifics of the origin of the petroleum, which is related to source deposits with humic type of organic matter of Mesozoic age, and to the high levels of catagenic transformation of the organic matter in the Paleozoic deposits.

A somewhat elevated content of vanadium (up to 90 g/t) and nickel is observed only on the eastern edge of the North Caspian Basin, in Bozoba, Kumsay, and other heavy-oil fields .

Among the other oil and gas basins in the former Soviet Union, the Surkhan-Vakhsh province stands out in metal concentration; here, a number of heavy-oil fields (Khaudag, Kokayty, and others), confined to the southern part of the Afghan-Tadzhik Basin, have high concentrations of vanadium (up to 975 g/t) and nickel (up to 195 g/t), and relatively high concentrations of molybdenum (up to 15 g/t). On the basis of the conditions of accumulation, these deposits probably are of the secondary-concentration type. The reserves of highly vanadiferous petroleum in the province are extremely limited.

The Khaudag Field is of greatest interest. It contains a pool of highly vanadiferous heavy oil in the Paleogene Bukharskiye beds, at a depth of 168–235 m, and probably can be worked underground.

In addition, 22 accumulations of bitumens have been found in the province which, on the basis of the conditions of their formation, may contain high concentrations of metals (V, Ni, Mo, possibly Re, and others).

The Olenek bitumen deposit (maltha and asphalt) in the Lena-Anabar province, with bitumen resources of 1.3 billion tons in the Permian, is the largest in Russia. In addition, accumulations of bitumen have been found on the Olenek arch in Vendian-Lower Cambrian deposits and at the top of the Upper Cambrian Lapar Formation deposits. The Permian and Upper Cambrian deposits contain 140–200 g/t vanadium, 44–87 g/t nickel, and 1.1–2.5 g/t molybdenum; in concentration of these metals, as well as in the conditions of their accumulation (supergene-residual subtype), they are analogous to the bitumen deposits of the Canadian asphalt belt (Figures 4.8–4.10). The vanadium resources in the Permian bitumens of the Olenek deposit can be estimated at 182,000 tons. However, because of the low bitumen concentration in the rock (average 2.9 percent), extraction of vanadium hardly seems feasible. Only in isolated sectors with intensive bitumen saturation ($\geq$57 wt%) is there any possibility of extracting vanadium in the refining of the bitumen, as is done in the case of the Athabasca oil sand deposit in Canada.

Other naphthometallogenic provinces in the former Soviet Union, where metalliferous deposits might be found, include: (1) the Indolo-Kuban depression in the North Caucasus, with deposits of heavy oil and maltha (Akhtyr-Bugundyr, Zybza, and others), carrying relatively high concentrations of Cd, Au, and Sr; and (2) the Middle Ob' (northern part of Surgut arch), where relatively high concentrations of vanadium and other metals in the petroleum have been found in isolated layers in the Valanginian and Hauterivian in the Mamontovskoye and West Surgut Fields.

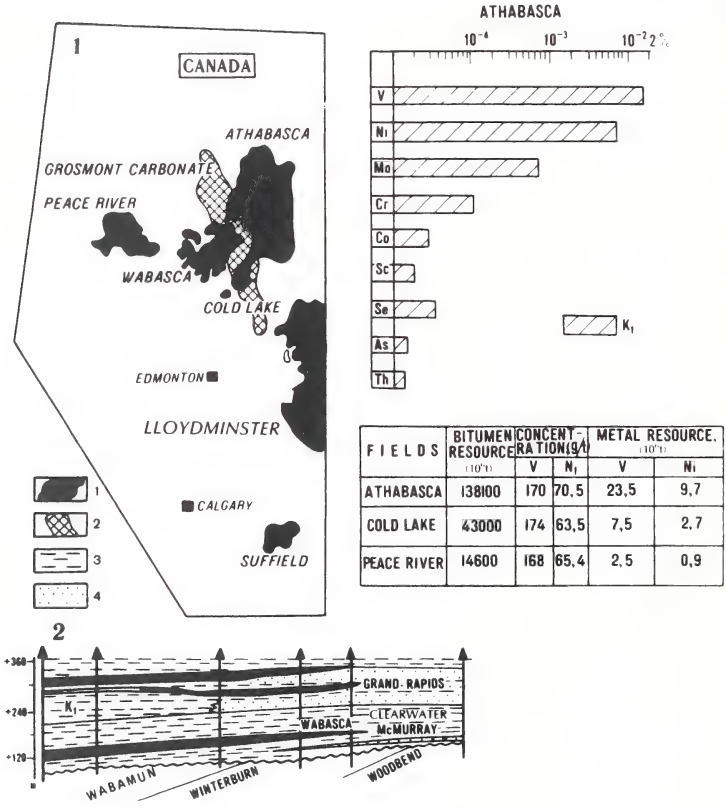
However, for the former Soviet Union as a whole, the most promising territory for prospecting for V and Ni in deposits of heavy oil and natural bitumens is the Volga-Urals province.

Most of the resources of vanadium in petroleum, and by far the largest part of the vanadium and nickel resources in natural bitumens, are related to this province.

4.2 SOUTH AMERICA

Eastern Venezuela Province

The Eastern Venezuela (Orinoco) oil and gas basin is confined to the zone where the Andean folded region meets the Precambrian Brazilian craton. The regional oil- and gas-bearing rocks are of Oligocene-Miocene age. The more than 250 known economic hydrocarbon deposits are confined to six main oil and gas districts: Las Mercedes, Anaco, Oficina, Temblador, Jusepin, and the so-called



FIELDS	BITUMEN RESOURCE (10^9t)	CONCENTRATION (g/t)		METAL RESOURCE, (10^3t)	
		V	N_i	V	N_i
ATHABASCA	138100	170	70,5	23,5	9,7
COLD LAKE	43000	174	63,5	7,5	2,7
PEACE RIVER	14600	168	65,4	2,5	0,9

FIGURE 4.8

Major oil sand deposits of Alberta, Canada (1), cross section through the Wabasca deposit (2), and trace metal concentration [after Jardine, 1974, and Alberta Oil Sands Technology and Research Authority]

1 – Oil fields and bitumen deposits in Cretaceous (K_1) sands
2 – Carbonate deposit
3 – Clay
4 – Sandstone

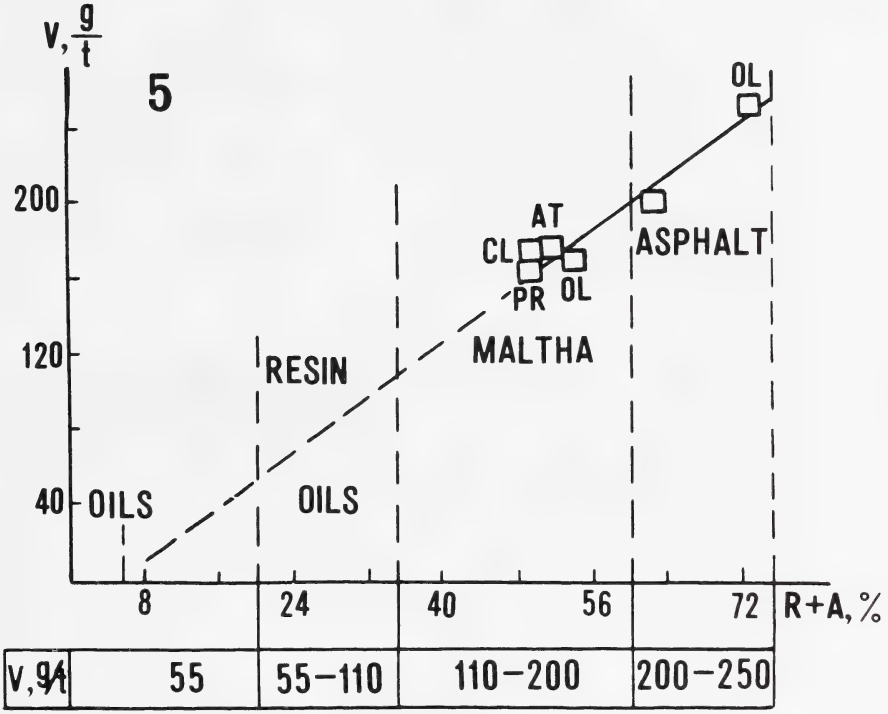


FIGURE 4.9

Vanadium content as a function of resin–asphaltene concentrations in selected bitumen deposits of Alberta, Canada and the former Soviet Union

AT – Athabasca
CL – Cold Lake
PR – Peace River
OL – Olenek

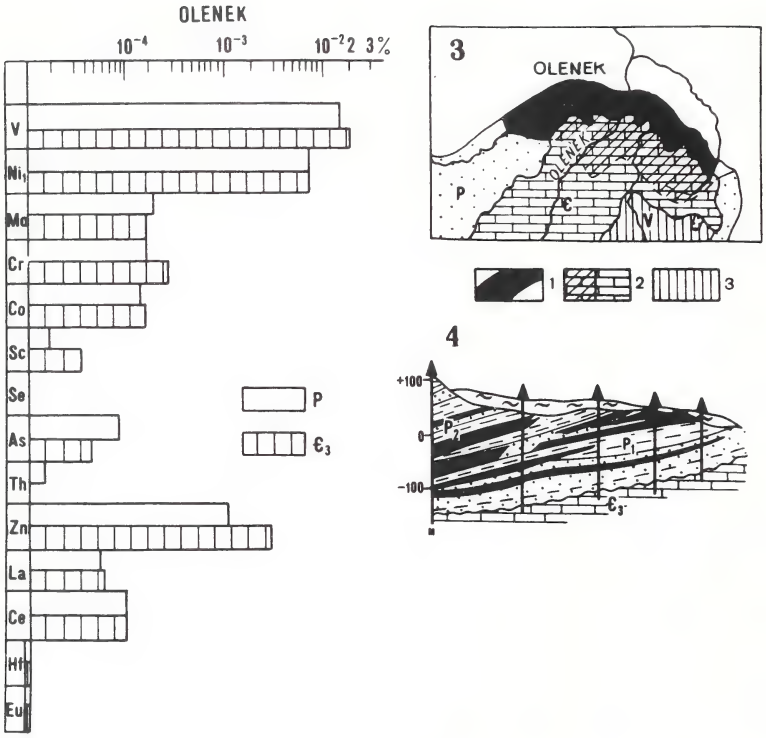


FIGURE 4.10

Map of Olenek deposit (3) and cross section (4) through the Ust-Bursk district, based on drilling results [after Ivanov, 1979] and trace metal concentration

1 – Pools in Permian sandstones

2 – Pools in Upper Cambrian carbonates

3 – Upper Precambrian Vendian sediments

Orinoco Oil Belt, which contains the world's largest reserves of extra-heavy (0.98–1.02 g/cm^3), vanadium-rich (360–490 g/t) crude. The Orinoco Oil Belt occupies an area of 600 × 50 km; the geologic reserves of extra-heavy oil are estimated at 191 billion tons, and of extractable oil, 43 billion tons.

A typical feature of the Orinoco basin, which governed the accumulation of heavy and extra-heavy oil as well as the vanadium contained in them, is the presence of outcrops, at the junction between the sedimentary cover and the Guiana shield, of rocks that allowed fresh waters of an oxidizing environment to infiltrate into the north-dipping sandy producing formations. This explains the occurrence of fresh and slightly salty waters, of the sodium bicarbonate type, in the producing Oligocene-Miocene complex over a considerable area on the south edge of the basin (Morozov, 1989). It is important to emphasize that in the catchment area of the infiltrating waters, on the Guiana shield, there are vanadiferous iron ores and titanomagnetite, including economic vanadium deposits. Interaction of infiltrating waters containing vanadium in anionic form $(VO_4)^{-3}$ with petroleum could have led, on the one hand, to oxidation of the petroleum, and on the other, to the formation of sulfur compounds of MeS type (V_2O_5), which are easily soluble in petroleum and form stable compounds with the asphalt-resin components, under the influence of reducing agents (S, H_2S). As was mentioned above, the reality of that process has been demonstrated on the basis of model experiments (Chakhmakhchev, Punanova, and Lositskaya, 1984).

On the whole, the extent of alteration of the oils in the Orinoco Basin changes from south to north, toward the central part of the basin, from 0.98–1.02 g/cm^3 (Orinoco belt) to 0.90–0.98 g/cm^3 in the Jobo, Temblador, and other fields and to 0.82–0.90 g/cm^3 in the Oficina Field. In this same direction, the contours of mineralization of the waters in the Paleogene deposits increase from 1 g/l or less to 10–15 g/l. The catchment area of the waters infiltrating the regional oil and gas reservoirs is also located on the north edge of the Orinoco basin, in the region of the Quiriquire field.

Over all, the distribution of vanadium concentrations in the petroleum are in accordance with the change in density of the oil and mineralization of the waters (Figure 4.11). The zones where petroleum containing more than 50–70 g/t vanadium occurs are bounded by the 10–12 g/l mineralization contours, and the zones of highly vanadiferous petroleum, those containing more than 200–250 g/t, by the <5 g/l contour.

The relationships between [V] and [A + R], [Ni], and [S] that we calculated on the basis of analytical data indicate two types of relationships (Figure 4.12). The crude oils of the central part of the basin, which were not subjected to the action of infiltrating waters, show a linear relationship between [V] and the above parameters that is typical of deposits of the organophilic type:

(13) $[V] = 233 \cdot \rho - 186.7$

(14) $[V] = 0.4 \cdot [Ni] + 16$

(15) $[V] = 90 \cdot [S] - 14$

The calculations show that maximum concentrations of primary vanadium in this petroleum cannot exceed an average of 47 g/t, for crude oil with a density of 9°API (1.0037 g/cm^3). With density values of 9–16°API (1.0037–0.9556 g/cm^3), the vanadium concentration may be 47–36 g/t, and for densities of 16–25°API, it may be 36–23 g/t (Figure 4.12).

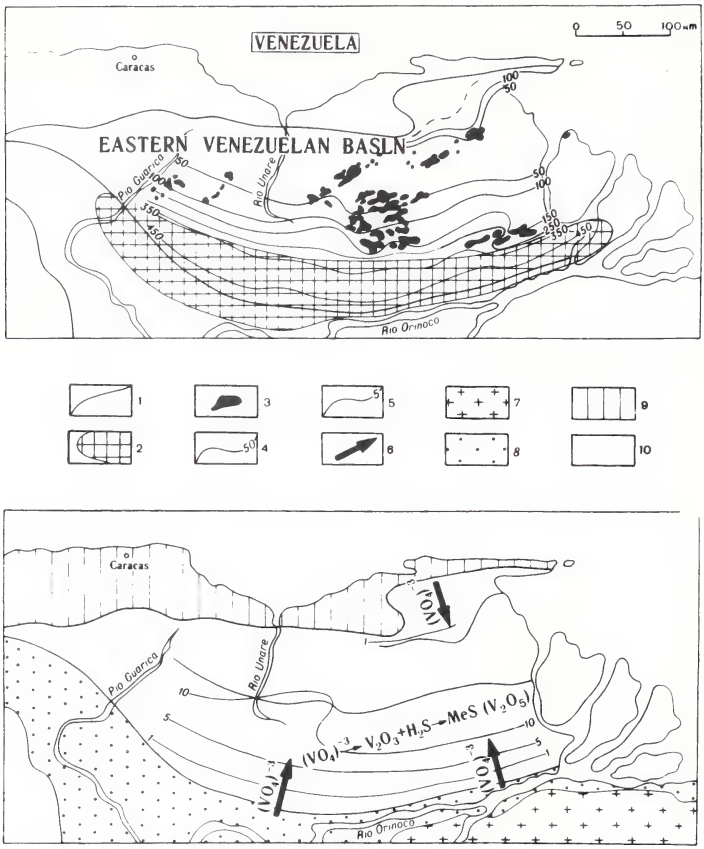
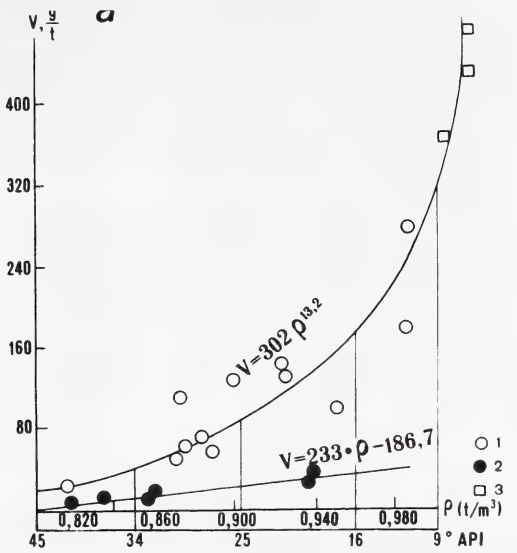


FIGURE 4.11

Vanadium-bearing petroleum and bitumen in the Eastern Venezuela Basin

1 – Boundaries of oil basins
2 – Orinoco Oil Belt
3 – Oil fields
4 – Isopleths of vanadium in petroleum and bitumen (g/t)
5 – Isopleths of mineralization of waters in Paleogene sediments (g/l)
6 – Direction of flow of infiltrating water
7 – Precambrian basement
8 – Precambrian basement below thin sedimentary cover
9 – Alpine folded complex
10 – Zones of occurrence of secondarily-enriched vanadium-bearing petroleum and bitumen



1	V, g/t	40	40–84	84–168	168–300	> 300
2		11,5	11,5–23	23–36	36–47	47–64

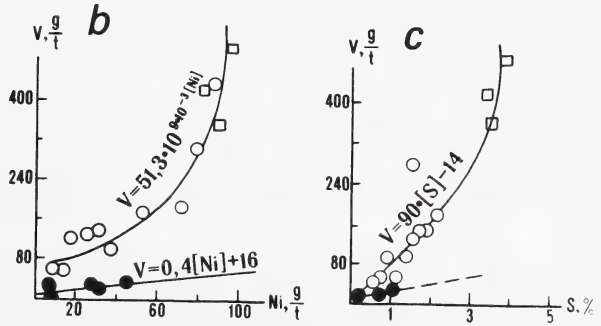


FIGURE 4.12

Vanadium concentration in the Eastern Venezuela Basin as a function of oil and bitumen density (a), nickel content (b), and sulfur content (c)

1 – Oil secondarily enriched in vanadium

2 – Oil containing primary vanadium

3 – Bitumen secondarily enriched in vanadium

For petroleum found in the sphere of action of slightly mineralized infiltrating waters, chiefly on the southern edge of the Orinoco Basin, the relationship between vanadium concentration and the physicochemical parameters of the petroleum is exponential, typical of deposits of the secondarily concentrated type. According to our calculations, the concentration of secondary vanadium in heavy oil, with a density of 9–16°API, is 168–300 g/t, and in extra-heavy oil, more than 300 g/t. The calculated and analytical data on vanadium and nickel concentrations in the petroleum of the Orinoco Basin are fairly close. This enables us to predict vanadium and nickel concentrations in fields for which we have no analytical data (Table 4.10).

The proposed scheme of accumulation of vanadium in heavy oils of the Orinoco Basin is inconsistent with the ideas of Kapo (1978) on the origin of the vanadiferous and nickeliferous petroleum of Venezuela. According to Kapo (1978), the metals were leached out of rocks enriched in vanadium and nickel in the Andean belt, and accumulated in the sediments along with the organic matter which later generated the hydrocarbons. In the case of organophilic vanadiferous deposits of heavy oil, in Kapo's (1978) scheme, the analytical relationships would be different from those we have considered above.

Maracaibo Province

Structurally, the Maracaibo Basin is an intermontane basin with a central massif, bounded by two lines of the Alpine mountain belt: the Andes and Sierra de Perijá on the west and the Cordillera de Mérida and Falcón-Lara on the south and east (Bockmeulen, Barker, and Dickey, 1983).

More than 70 economic fields have been discovered in the basin (Figure 4.13). They are related to Cretaceous and Paleocene-Miocene deposits, the latter being exposed within the basin, allowing infiltrating waters to penetrate into the sandy producing formations, which are of wide areal extent and highly permeable. According to Bockmeulen, Barker, and Dickey (1983), the economic accumulations of petroleum in the Paleogene-Neogene deposits are distributed in the vicinity of fresh and slightly saline waters over virtually the whole area of the Maracaibo basin. Within the giant Bolívar Coastal zone of accumulation of heavy oil, including the Tia Juana, Lagunillas, and Bachaquero Fields, the waters in the Eocene and Miocene have a salinity of only 0.6 to 0.9 g/l. A systematic increase in density of the petroleum in the direction of the catchment area of the infiltrating waters is found, related to the oxidizing effect on the petroleum of microorganisms, sulfates, and oxygen in the water (Morozov, 1989).

As in the Orinoco basin, the distribution of vanadium concentrations corresponds, on the whole, to the variation in density of the petroleum and mineralization of the waters (Figure 4.13). The zones containing heavy oil with more than 150 g/t vanadium are bounded by mineralization contours on the order of 5 g/l. In individual fields in zones with fresh water, where crudes with various densities are observed, from light to medium and extra-heavy, as in the case of the Bolívar Coastal and Cabimas Fields, the concentrations of vanadium in the petroleum vary correspondingly.

On the basis of these relationships between vanadium concentration and petroleum density and sulfur content, and between [V] and [Ni], two types of petroleum were found, with respect to vanadium. In the first type, chiefly light and medium petroleum, a linear relationship is found between V and the parameters in question, reflecting the organophilic nature of the metals (Figure 4.14):

TABLE 4.10
Analytical and calculated vanadium and nickel concentrations in the extra-heavy oil from the Orinoco Oil Belt of the Eastern Venezuela Basin

Elements	Density of oil		Concentration (g/t)			
	°API gravity	ρ_4^{20} (g/cm^3)	Analytical		Calculated	
			V	Ni	V	Ni
Dacion	21.8	0.9192	133	29	120	30
Merey	12.4	0.9798	250		240	62
Oscurote, Norte	19.2	0.9351	187		155	50
Oficina	22.6	0.9182	129		115	20
Arecuna	11.2	0.9881			260	60–65
Bare	10.3	0.9944			280	68
Jobo	11.0	0.9926	278	81	270	80
Morichal	8.70	1.0059	310	90	300	85
Tacat	18.2	0.9415			140	40
Temblador	19.5	0.9332			120–130	30–40
Pilon	12.3	0.9805	181	72	175	60
Cerro Negro	8.60	1.0066	460	84	470	90

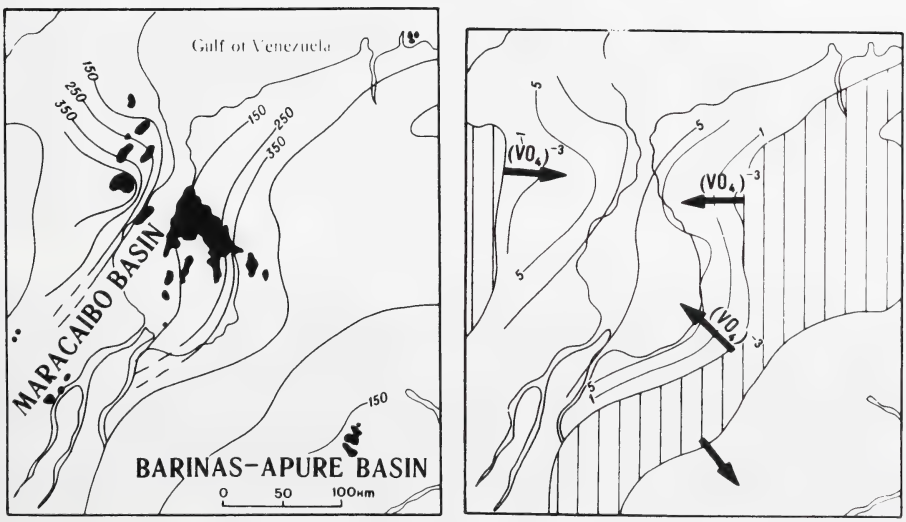
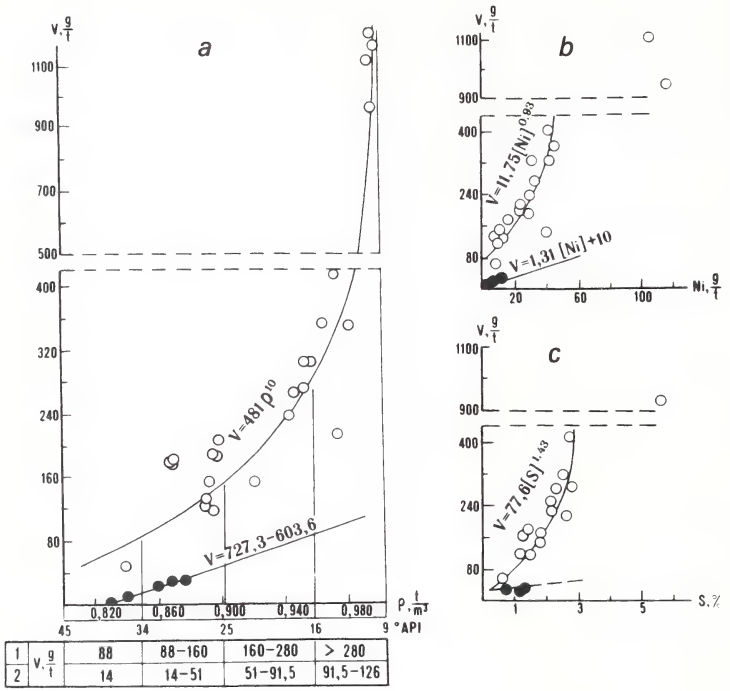


FIGURE 4.13
Vanadium-bearing petroleum in the Maracaibo Basin (for legend, see Figure 4.11)



1	V, g/t	88	88–160	160–280	> 280
2		14	14–51	51–91,5	91,5–126

FIGURE 4.14

Vanadium concentration in the Maracaibo Basin as a function of oil density (a), nickel concentration (b), and sulfur concentration (c) (for legend, see Figure 4.12)

(16) $[V] = 727.3 \cdot \rho - 603.6$

(17) $[V] = 1.31 \cdot [Ni] + 10$

Calculations show that as the density of this type of petroleum increases 16–9°API (0.9556–1.0037 g/cm^3), the vanadium concentration may reach an average of 90–126 g/t because of residual accumulation of the metalliferous asphalt-resin fractions. This is 2.5 times higher than the primary vanadium content in the petroleum of the Orinoco Basin. This probably is related to the presence in the section of highly carbonaceous domanik-type rocks, with sapropelic organic matter and an elevated content of metalloporphyrins (as much as 5590 mg/100 g of bitumoid) and metals. The Turonian-Coniacian La Luna formation, considered by most investigators to be a petroleum-generating source bed, is such rock.

The second type of vanadiferous petroleum occurs chiefly in heavily oxidized petroleum under the influence of fresh infiltrating waters. The relationship between [V] and density, [S], and [Ni] is

nonlinear, with a sharp increase in vanadium concentration from 280 to 1200 g/t in a relatively narrow interval of variation in density of the petroleum (Figure 4.14). In this case, the maximum concentration of vanadium is related to the petroleum with the highest sulfur content (5.5 percent S).

The source of the vanadium, which is transportable by infiltrating water in an oxidizing environment, apparently lies within the catchment areas of the water. These areas are found within the folded rim of the Andean ore belt, with which economic deposits of vanadium and fairly numerous accumulations of highly vanadiferous solid bitumens are associated in Peru and Argentina.

It can be assumed that the total concentration of vanadium in the heavy oils of the Maracaibo basin is made up of two components, primary and introduced. In particular, fragments of primary vanadium are indicated by the relatively high content of vanadyl porphyrins, with maximum concentrations, in the Boscan Field, of as much as 354–372 mg/100 g .

The high concentration of vanadium in some heavy oil fields in the Maracaibo province with large petroleum reserves suggests that they should be considered major vanadium deposits. For instance, in the Boscan Field, with initial extractable oil reserves of 166.4 million tons, the extractable vanadium reserves are 155,000 tons, with an average content of 937 g/t of the metal. According to our calculations, the vanadium lost in refining (as of 1988) amounts to 47,800 tons. In the fields of the Bolívar Coastal zone, the initial extractable reserves of vanadium were on the order of 1,200,000 tons, and the initial geologic reserves of vanadium, on the order of 345,000 tons.

A unique combination of geological and geochemical factors, which on the one hand caused the accumulation of huge masses of petroleum and, on the other, the possibility of concentrating vanadium in them, puts the Orinoco and Maracaibo Basins in the category of geologic phenomena.

In addition, the ascertained patterns of accumulation of vanadium in the heavy oil in these basins make it possible to predict zones of occurrence and concentration of the metal in similar geological and geochemical settings.

In South America, a group of oil and gas basins confined, like the Orinoco Basin, to regions of subsidence at the junction of the Brazilian craton and folded regions, can be considered promising with respect to vanadiferous heavy oils and bitumens. Such basins include the Barinas-Apure (Venezuela), Upper Amazon (Colombian, Ecuador, and Peru), and the Upper and Middle Magdalena (Colombia), which, like the Maracaibo Basin, is related to intra-fold regions of subsidence. In addition, the intra-cratonic regions of subsidence marginal to the Guiana shield may prove to be vanadiferous (Figure 4.15).

Upper Amazon Province

The possibly vanadiferous Upper Amazon oil and gas basin is situated in the zone between the Andes Alpine folded region (Eastern Cordillera) and the Precambrian Brazilian craton. The main producing horizons are the Lower Cretaceous sandstones of the Caballos and Olin formations, infiltrated by fresh waters with an average mineralization of 0.7 g/l. Outcrops of rocks on the east flank of the Andean fold belt are the catchment area for these infiltrating waters (De Righi and Bloomer, 1976). Another freshwater catchment area is related to the contact between the sedimentary and crystalline rocks of the Guiana shield (Orinoco type). These hydrogeological features of the basin make it possible for vanadium to be introduced with fresh water from the regions from which it is discharged and to accumulate in the petroleum due to its reaction with the infiltrating water. The

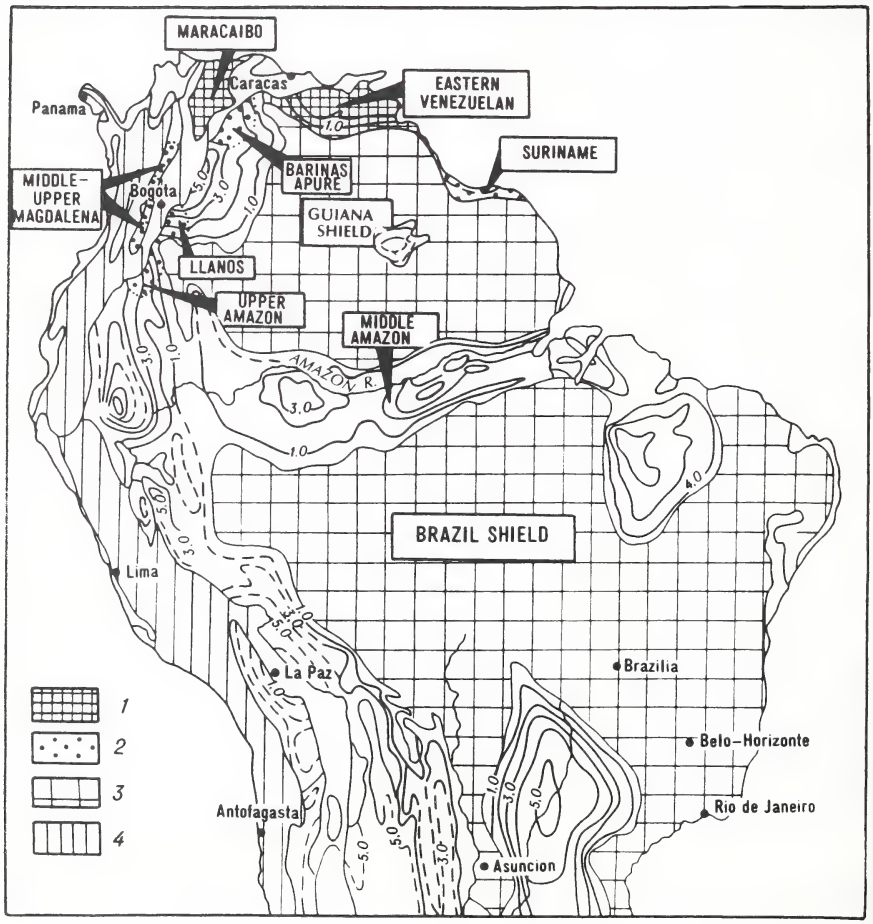


FIGURE 4.15

Metalliferous heavy crude oil and bitumen prediction for South America [Compiler: I.S. Goldberg]; structure contours on top of the basement (dashed where estimated); contour interval, 1 km

1 – Basins with economic metalliferous oil and bitumen deposits

2 – Basins with potential metalliferous heavy crude oil and bitumen

3 – Precambrian basement rocks

4 – Folded zones

existence of deposits of heavy and extra-heavy oil and bitumen in these zones of infiltrating waters, including those close to the contact between the sedimentary cover and the Precambrian shield, is an extremely favorable prerequisite for finding vanadiferous heavy oil and bitumen. Above all, this pertains to the bitumen accumulations in the Eocene sandstones in the eastern part of the Putumayo River valley in Colombia, near the boundary between the sedimentary cover and the Precambrian shield (De Righi and Bloomer, 1976); the shallow accumulations of heavy (0.946–1.00 g/cm^3) oil and maltha in Ecuador ("Pungarayacu" zones); and the heavy oil fields in the Lower Cretaceous deposits of Ecuador and Peru (Figures 4.16–4.19 and Table 4.11).

On the basis of the ascertained relationships between the vanadium content and the physicochemical parameters of the petroleum for the Orinoco basin, we calculated a predicted concentration of the metal for the heavy oil deposits of that basin (Figure 4.12).

A similar prediction of the vanadium concentration in heavy oil, but by analogy with the Maracaibo Province, was made for the Upper and Middle Magdalena and Llanos Basins (Colombia) (Figures 4.18 and 4.19, Table 4.11). In addition, we should mention the existence of highly vanadiferous (2600–10,900 g/t V) solid bitumen in the Andes fold belt of the Western Cordillera in Peru and Argentina. In the 1930s, one vanadiferous bitumen vein in Peru, near Cerro de Pasco, yielded about 80 percent of the world production of vanadium. This bitumen vein, about 5 m thick, lies on either side of a rhyolite dike intruding Neocomian rocks. Because of the thermal effect of the intrusion, the bitumens were transformed into unique carbon compounds. In the outer part of the vein, the bitumen is kiskeite (high-sulfur anthraxolite), containing 65 percent V_2O_5 and 7.5 percent NiO in the ash; in the central part, natronite (vanadium sulfide); and in the zone between, petroleum coke. These vanadiferous bitumens can be considered to be remnants of a single Andean ore and petroleum belt.

4.3 NORTH AMERICA

Western Canada Province

The Western Canada oil and gas basin is confined to the zone of junction between the old North American craton and the fold-block geosynclinal system of the Cordillera. The economic oil and gas potential is related to Devonian, Mississippian, Pennsylvanian, and Cretaceous deposits.

In the eastern and northeastern parts of the basin, the so-called Canadian oil sand belt can be traced for more than 600 km along the flank of the Canadian shield. It contains giant accumulations of bitumen in the Lower Cretaceous deposits, with total reserves of 214.6 billion tons (Figure 4.8). Data on the geology and geochemistry of these bitumens are given in numerous publications (Jardine, 1974; Deroo *et al.*, 1974; McConville, 1975, and Jacobs, Bachelor, and Filby, 1984).

The Athabasca deposit is controlled by a zone in which the highly porous (30–35 percent) and permeable McMurray sands (Lower Cretaceous) pinch out. These strata consist successively of fluvial, delta-front, and near-shore marine sands. Their thickness increases northward from the pinch-out zone to 60 m or more, sometimes reaching 8090 m. The average bitumen content of the deposit is 7.8 wt%, reaching maximums of 18–20 wt%. The bitumen reserves are estimated to be 138.1 billion tons.

The Peace River deposit is controlled by a huge lithostratigraphic trap on the Peace River monoclinal slope. The trap is related to the pinch-out of continental sandstones of the lower Mannville group, which lie on the eroded surface of Permian, Triassic, and Jurassic deposits. Depths to the producing deposits range from 450 to 800 m. The average bitumen saturation is 7.25 wt%; the geologic reserves are 14.6 billion tons.

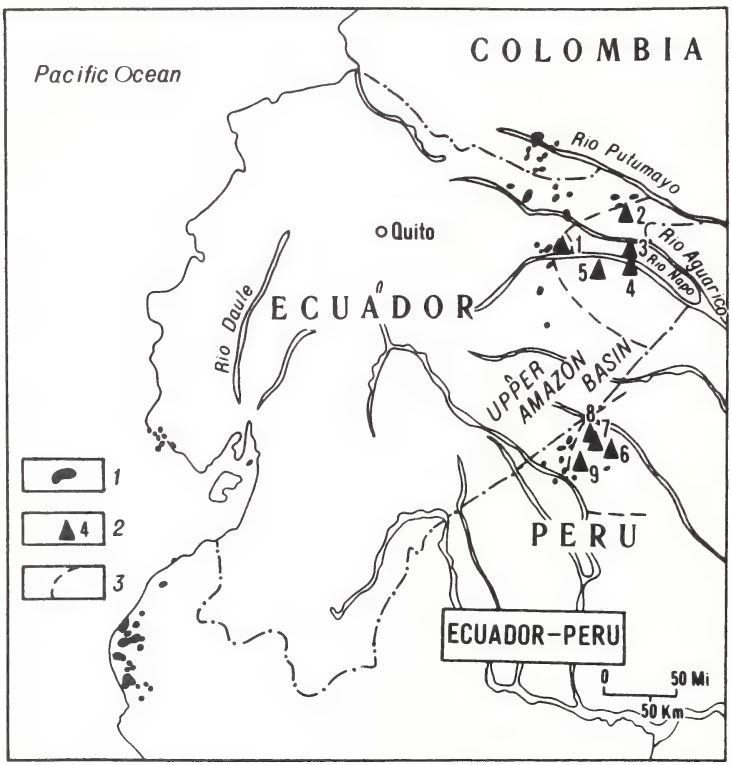


FIGURE 4.16

Vanadium concentration in heavy crude oil in the petroliferous basins of Ecuador and Peru [Compiler: I.S. Goldberg]

1 – Oil fields

2 – Heavy crude oil

3 – Zones of heavy crude oil with presumed high vanadium content

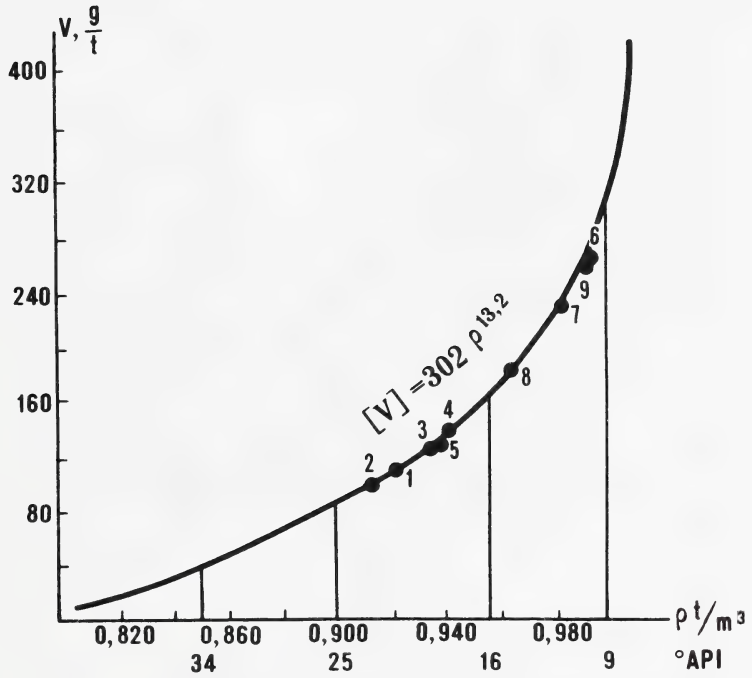


FIGURE 4.17
Vanadium content as a function of density in petroliferous basins of Ecuador and Peru

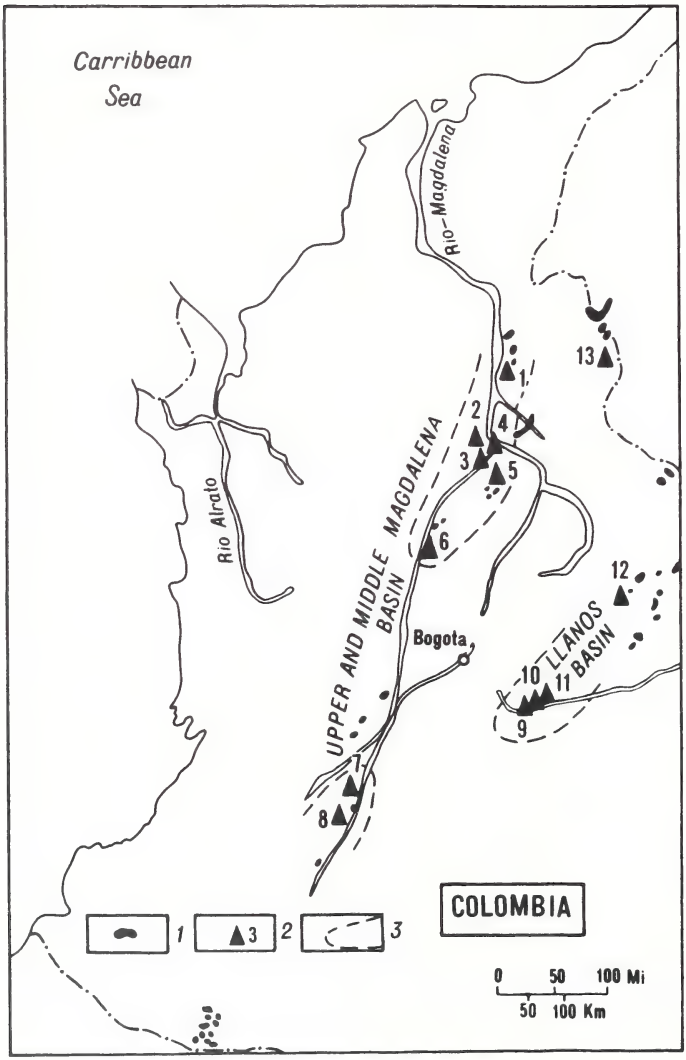


FIGURE 4.18

Vanadium concentration in heavy crude oil in the petroliferous basins of Colombia [Compiler: I.S. Goldberg]

1 – Oil fields

2 – Heavy crude oil

3 – Zones of heavy crude oil with presumed high vanadium content

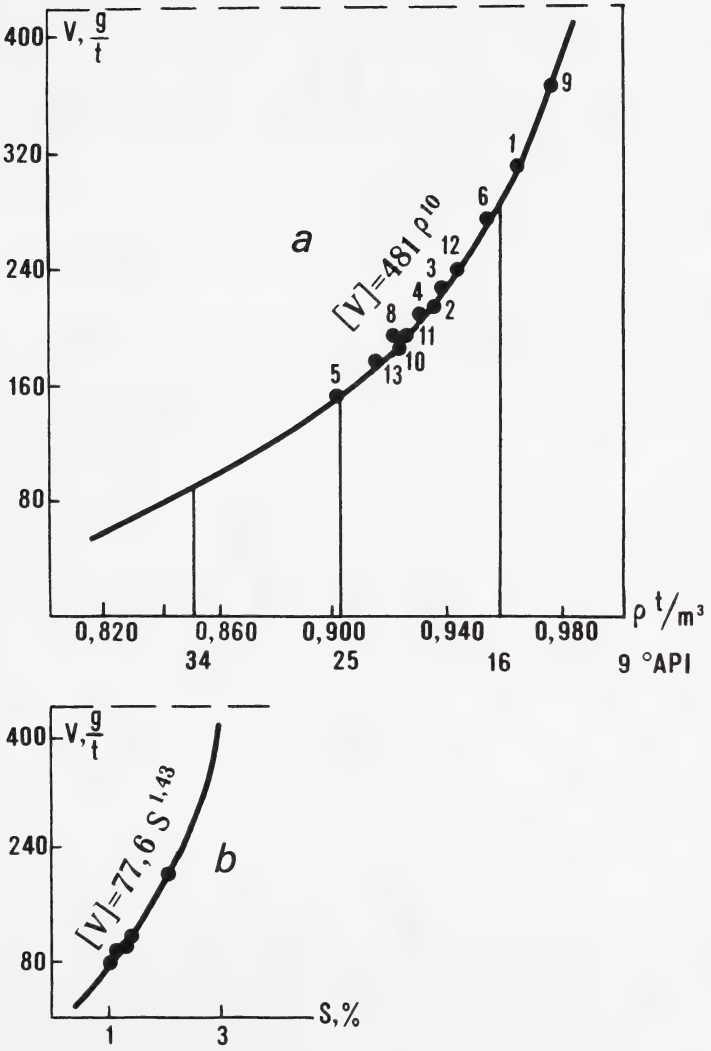


FIGURE 4.19

Vanadium content of heavy crude oil in basins of Colombia as a function of density (a) and sulfur content (b)

TABLE 4.11
Estimated resources of vanadium in heavy oil from Colombia, Ecuador, and Peru
[Compiled by I.S. Goldberg]; map locations: Ecuador and Peru, Figure 4.16; Colombia, Figure 4.18

Map number	Oilfield	Age/Depth (m)	Oil			Prognosis	
			ρ (t/m^3)	S (%)	Coke (%)	V (g/t)	Resources V_2O_5 (10^3 t)
			Ecuador				
1	Auguarico	–	0.921			100–110	
2	Fanny	–	0.915			100	
3	Mariann	–	0.934			120	
4	Yuturi	K/2206	0.940			130	
5	Tivacuno	K/2419–2785	0.930			120	
	Zones "Pungarayacu"	270	0.946–1.000			140–280	160
			Peru				
6	Barta	2400–2720	0.990			240–250	23
7	San Jacinto	2194–2423	0.979			220–230	
8	Shiviuacu	2774–2835	0.965			180	
9	Jibaro	3081–3400	0.990			240–250	
			Colombia				
1	Tisquirama	P_1/1524–1649	0.965			280–300	
2	Cataglio	P_2/1910	0.935	1.98	10.1	200–220	
3	Galan	P_3/1098	0.936	1.11	8.4	200	
4	Casabe	P_3/769–1360	0.930	1.08	7.5	180–200	10.5
5	Lasira-Infantas	P_2/977	0.908	0.96	6.4	100	11.5
6	Velasquez-Palagua	P_2/2154–2163	0.914–0.953	1.03	6.3	100–130 260–280	9.0
7	Dina	P	0.918	–	–	100–130	
8	Tello	P	0.932	–	–	200	
9	Castillo	P-K	0.976	–	–	340–360	
10,11	Guariba, Apiay	P-K	0.936	–	–	200	
12	La Gloria	P-K	0.946	–	–	220–240	
13	Carbonera	P_2/590	0.920	–	–	160–180	

In the Wabasca Field (Figure 4.8), the bitumen deposits are related to the sands of the Wabasca and Grand Rapids Formations, separated by a 90-meter thickness of marine clays of the Clearwater Formation. The average bitumen content is 6.9 wt% and the reserves are 18.9 billion tons.

Down the monoclinal dip from the flanks of the Canadian shield toward the central part of the basin, the bitumen deposits in the Lower Cretaceous are superseded by oil fields with gradually decreasing bitumen density: Athabasca, 1.0291–1.0143 g/cm^3, Wabasca, 1.000–0.9792 g/cm^3, Lloydminster, 0.9593 g/cm^3, Wainwright, 0.915 g/cm^3, Bellhill Lake, 0.8984 g/cm^3, and Pembina, 0.849 g/cm^3.

From the results of the investigations that have been made (Scott, Collins, and Hodgson, 1954; Jacobs, Bachelor, and Filby, 1984), a linear relationship is found between the V concentration and the density of the petroleum and bitumen and the content of sulfur and coke, and also between [V] and [Ni]. These relationships persist continuously through the whole series, from light to heavy oil and bitumen. As was mentioned earlier, such analytical relationships are typical of the organophilic type of concentration of metals in petroleum and bitumen.

Maximum concentrations of V (average 168–174 g/t), Ni (63.5–70.5 g/t), Mo (5.1–7.2 g/t), Cr (0.1–1.0 g/t), Co (0.2–0.4 g/t), Ga (0.2–0.36 g/t), and other elements are found in the bitumen of the Canadian oil sands deposits. In connection with the huge bitumen reserves, even when the vanadium and nickel concentrations are relatively low, the resources of these metals are 23.5 and 9.7 million tons, respectively, in the Athabasca deposit, 7.5 and 2.7 million tons in the Cold Lake deposit, and 2.5 and 0.9 million tons in the Peace River deposit (Figure 4.8).

Ascertaining the conditions of accumulation of vanadium and nickel in the bitumen of the Canadian belt is related to solving problems of the origin of the Lower Cretaceous petroleum and the factors that caused it to be transformed into asphaltic bitumen. Deroo *et al.* (1974) traced the whole evolutionary series of geochemical changes of the Cretaceous petroleum, from the center of the Western Canada Basin to the bitumen on its periphery, which made it possible to postulate their genetic unity. The process of transformation of the series, petroleum → heavy oil → bitumen, is related to the following factors: (1) biogenic oxidation leading to the gradual disappearance from the petroleum of, first, *n*-alkanes, then, isoprenoids; (2) solution in formation waters, leading to loss of light hydrocarbons of all types; and (3) abiogenic oxidation. At the same time, the reasons why these deposits have been preserved, when the rocks of all stratigraphic subdivisions of the Cretaceous are exposed adjacent to outcrops of the Precambrian shield, still remain unclear. If we accept the point of view that the transformation of normal into heavy, highly viscous petroleum occurred along the paths of petroleum migration, due to the oxidizing effect of the infiltrating fresh waters contacting the petroleum encountered, and that the waters were derived from the magmatogenic vanadium deposits of the Precambrian shield, then we would expect the bitumens to be enriched in metals, particularly vanadium, as occurs in other such zones of infiltration (for example, in the Orinoco and Maracaibo Basins). However, that is not the case. Therefore, Gussow's (1955) model seems more likely: giant accumulations of normal oil with gas caps accumulated in the marginal parts of the basin in connection with earlier, more extensive development of the clays of the Clearwater Formation and overlying deposits, which could have overlain part of the Canadian shield. As a result of later erosion, the gas was dissipated but the petroleum, already in traps lying relatively close to the surface, was transformed into highly viscous petroleum and preserved. In this case, the accumulation of vanadium and nickel in the bitumen was proportional to the residual accumulation of the asphalt-resin components during supergene transformation of originally metalliferous, relatively light oils.

Data on the distribution of metals (V, Ni, Mo, *etc.*) by oil fractions in the bitumen (Table 4.12) supports this point of view.

In addition, Gussow's model is supported by the fact that the concentration of individual elements per unit of asphalt-resin substance, on the whole, remains constant . For instance, the concentration of V per unit of asphalt-resin substance is 325–358 g/t; of Ni, 130–135 g/t; and of Mo, 12–14 g/t. When the bitumens are refined, heavy metals are concentrated in the residue, whereas the synthetic petroleum is virtually devoid of these elements. According to Jervis, Ho, and Tiefenbach (1982), synthetic petroleum from the Canadian bitumen contains 0.002–0.007 g/t V, and from the maltha, 260 g/t V.

In rare element distribution and concentration, the Athabasca bitumen is virtually identical with the Permian bitumen of the Olenek deposit (Figures. 4.9 and 4.10), which probably means that they were formed under similar conditions.

TABLE 4.12
Fractional distribution of metals in bitumen from Alberta
[after Jacobs, Bachelor, and Filby, 1984] (percent)

Element	Oils	Resins	Oils plus resins	Asphaltenes
V	7.0	20.3		72.7
Ni	12.7	15.2		72.1
Mo	2.3	1.5		96.2
Se			51.2	48.8
As			36.8	63.2
Sb			13.0	87.0
Hg			32.2	67.8
Zn	–	–		–
Co			34.6	65.4
Cr	9.4	13.3		77.3
Sc			44.7	55.3
Ga			13.6	86.4

California Provinces

The oil and gas basins of California (the Great Valley and Salinas-Cayama [San Joaquin], Santa Maria, Ventura-Santa Barbara, Los Angeles, and others) (Figure 4.20) are related to graben-synclinoriums filled with Cretaceous to Holocene sediments. The main petroliferous formations are confined to Paleogene and Neogene sandy-shaly deposits, lying at depths from a few hundred to more than 5500 m. Heavy oil is found in virtually all basins, but those with the highest density and maximum sulfur content (2.5–5.0 percent) are found in the Miocene Santa Maria Valley, Orcutt, Cat Canyon, and Lompoc Fields of the Santa Maria Basin and in several Oligocene-Miocene Fields (Oxnard, West Montalvo, and others) of the Ventura-Santa Barbara Basin.

The relationships between between vanadium and nickel concentrations and density of the heavy oils of the Santa Maria Basin that we calculated on the basis of analytical data show that they are linear functions of the following type (Figure 4.21):

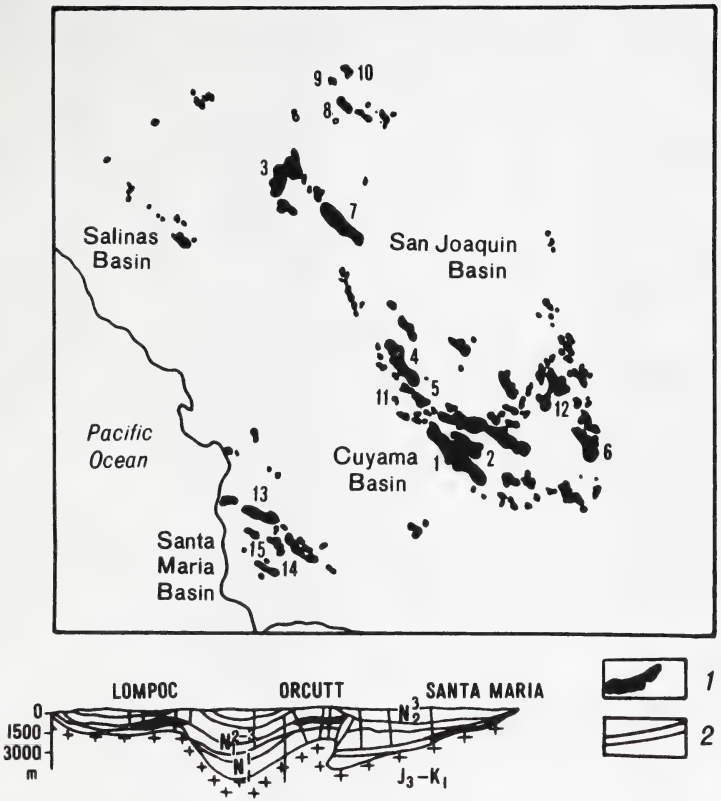


FIGURE 4.20

Schematic cross section and map showing location of oil fields in the San Joaquin Valley and adjacent areas, California

1 – Oil fields with known concentrations of vanadium and nickel

1. Midway-Sunset
2. Elk Hills
3. Coalinga
4. North Belridge
5. Coles Levee
6. Edison
7. Kettleman Dome
8. Helm
9. San Joaquin
10. Raisin City
11. Cymric
12. Kern River
13. Santa Maria
14. Lompoc
15. Orcutt

2 – Monterey Formation

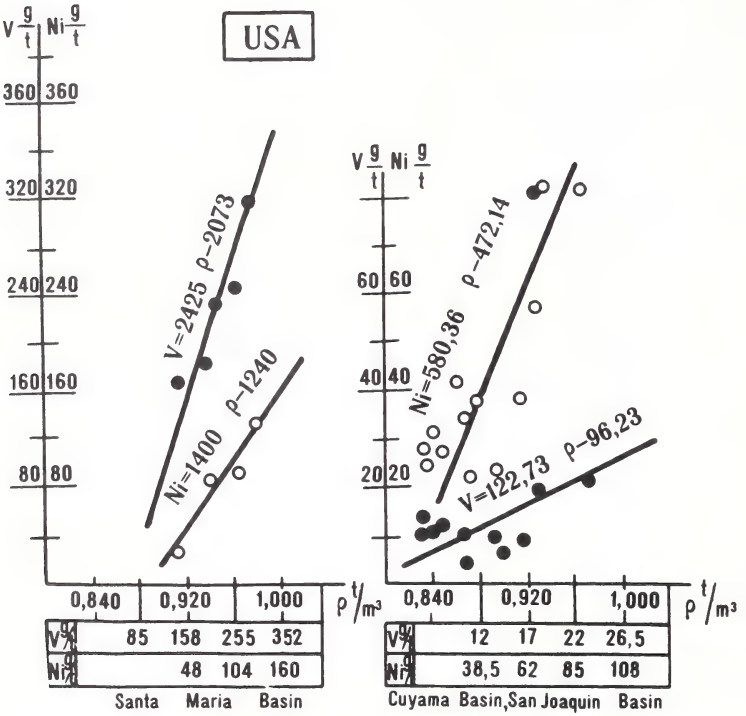


FIGURE 4.21
Vanadium and nickel concentrations as a function of density in the Santa Maria, Cuyama, and San Joaquin Basins

(18) $[V] = 2425 \cdot \rho - 2073$

(19) $[Ni] = 1400 \cdot \rho - 1240$

For the petroleum of the Great Valley [San Joaquin] Basin, which has a low sulfur concentration (0.200.88 percent), the relationship between [V] and [Ni] is the opposite, and is characterized by the following functions (Figure 4.21):

(20) $Ni] = 580.36 \cdot \rho - 472.14$

(21) $[V] = 122.73 \cdot \rho - 96.23$

The difference in concentration of metals in the various basins probably is the result of nonuniform conditions of petroleum formation, particularly the composition of the source rocks and the extent of catagenesis of the organic matter. In the Santa Maria Basin, the source of the petroleum could have been the diatomaceous shales of the Monterey and Cisco formations, in low stages of catagenesis, which led to the formation of high-cyclic petroleum that was initially heavy and enriched in heavy metals (early catagenic subtype). Analytical and calculated data on the concentration of V and Ni in such California petroleum are given in Table 4.13. During the development of such fields as the Orcott, Santa Maria Valley, and Cat Canyon, on the order of 20,600 tons of vanadium and 7,200 tons of nickel were recovered in 1988 as a by-product with the petroleum. The remaining reserves of these metals are about 3,300 tons of V and 1,300 tons of Ni.

The presence of elevated concentrations of Hg, As, Se, Sb, and Zn in some California crudes should be mentioned. In the Cymric Field in the Great Valley [San Joaquin] Basin, the content of mercury in the petroleum reaches 29.6 g/t, and that of zinc, 85.8 g/t, together with 30 g/t of vanadium and 43 g/t of nickel. Analysis of the partitioning of the metals by petroleum fraction (Yen, 1975) showed that 58.6 percent of the As, 2.8 percent of the Sb, 2.1 percent of the Hg, and 4.6 percent of the Zn are confined to the oil fractions. The resins contain 20.3 percent of the As, 7.2 percent of the Sb, 60 percent of the Hg, and 36.1 percent of the Zn, and the asphaltenes, 21.1 percent of the As, 90 percent of the Sb, 37.9 percent of the Hg, and 59.3 percent of the Zn.

Big Horn Province

In the Rocky Mountain oil and gas basins, which are intermontane basins of an epi-platform orogen, the main reserves of heavy (0.900–0.935 g/cm^3), high-sulfur (1.8–3.1 percent) petroleum are concentrated in the fields of the Big Horn Basin (Grass Creek, Hamilton Dome, Oregon Basin, Spring Creek, and others). These fields are grouped in anticlinal zones of petroleum accumulation on the western edge of the basin, in an environment of infiltrating fresh and slightly mineralized water. These waters are derived from catchment basins situated on the Absaroka volcanic plateau, as is shown by the drop in effective water pressure from the areas where the rocks crop out on the rim toward the axis of the basin.

Typically, it is on the western edge of the basin, in the Mississippian Madison and Pennsylvanian Tensleep Formations, as well as in the Triassic, that petroleum with a relatively high vanadium content (80–120 g/t) has been found. Figure 4.22 shows that the contours of vanadium concentration are parallel to outcrops of volcanic rocks on the rim, with the concentration decreasing toward the axial zone and zones of petroleum accumulation on the eastern limb. This trend probably reflects the penetration of meteoric waters carrying soluble vanadium compounds from the volcanic plateau, and highly permeable petroliferous formations where the petroleum was oxidized at the water-oil interface and vanadium accumulated in the petroleum at the same time. As follows from the graphs (Figure 4.23), secondary accumulation of vanadium in the petroleum could occur only in the case of certain boundary values of density (more than 0.920 g/cm^3) and sulfur content (more than 2.5–2.7 percent). This is emphasized by the change from the previous linear to logarithmic functions:

(22) $V] = 1100.0000 \cdot \rho - 928.0$

(23) $Lg[V] = 8.3750 \cdot \rho - 5.805$

TABLE 4.13
Analytical and calculated concentrations of vanadium and nickel in heavy oil from the coastal area of California

Field	Density of petroleum		Concentration (g/t)				V (in residue at 900°F)
	°API (gravity)	δ_4^{20} (g/cm^3)	Analytical		Calculated		
			V	Ni	V	Ni	
Santa Maria Valley	15.0	0.9623	180–280	97–130			380–595
Orcutt	23.0	0.9120	162.5	23			490
Cat Canyon	10–16.0	0.9966–0.9556			230	90	
Bradley Canyon	11.0	0.9926			320	140	
Oxnard	9.0	1.0038	403.5		382	165	640
Jesus Maria	9.0	1.0038			382	165	
Arroyo Grande	15.0	0.9623			260	105	
Nicolai			246.5				
Purisma			218.5				

FIGURE 4.22

Schematic cross section and map of vanadium-bearing petroleum in the Big Horn Basin, Wyoming

1 – Oil fields
1. Elk Basin
2. Garland
3. Byron
4. Oregon Basin
5. Spring Creek
6. Grass Creek
7. Hamilton Dome
8. Worland

2 – Isopleths of vanadium concentration in petroleum
3 – Direction of flow of infiltrating water
4 – Volcanic rocks
5 – Basement
6 – Boundary of oil basin
7 – Tensleep Formation
8 – Madison Formation
9 – Zones of occurrence of infiltrating waters

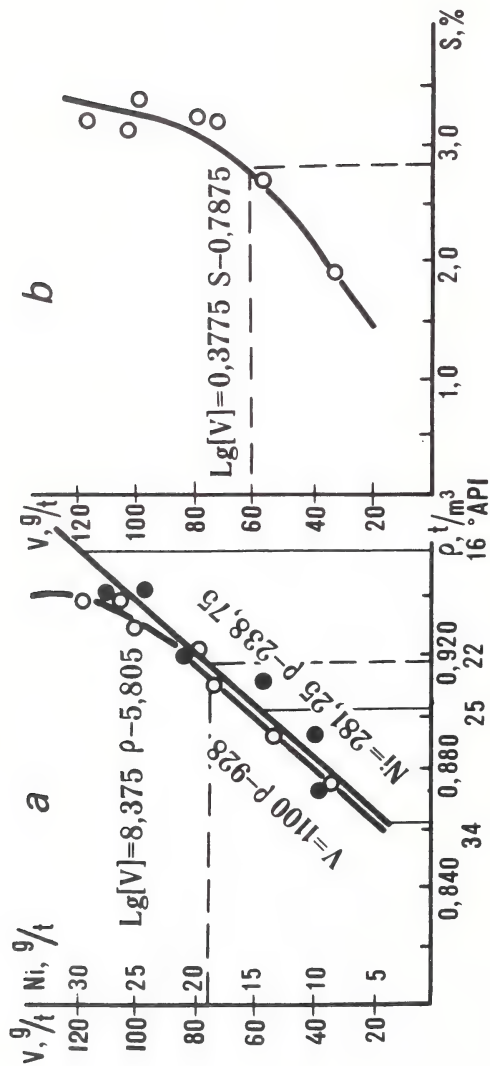


FIGURE 4.23
Vanadium and nickel concentrations as a function of oil density (a) and sulfur content (b) in the Big Horn Basin
1 – Vanadium
2 – Nickel

(24) $Lg[V] = 0.3775\ S - 0.7875$

In this case, vanadium enrichment of the oxidized heavy, high-sulfur petroleum was not accompanied by the introduction of nickel, as is seen from the linear relationship between [Ni] and density:

(25) $[Ni] = 281.25 \cdot \rho - 238.75$

According to available published data on the content of metals in the petroleum of various basins of the United States, no fields of heavy oil substantially enriched in V and Ni have been found, other than those mentioned above. Only isolated fields with heavy, high-sulfur petroleum with a relatively high vanadium content have been reported (Salt Creek, Tatum, and others).

4.4 EUROPE

Adriatic Province

The Adriatic oil and gas basin is part of the system of intermontane basins of Alpine folding and is situated between the Dinarides, the Apennines, and the Western and Central Alps. In Italy, pools of high-sulfur heavy oils (up to 7.9 percent S, 0.96–1.01 g/cm^3) are concentrated chiefly in areas of Cis-Apennine depressions, where they have accumulated in erosional highs of Cretaceous deposits. It can be assumed that such substantial alteration, and the increase in sulfur content of the Cretaceous petroleum, lying at depths up to 3000 m, was related to paleo-supergenesis that occurred at the Eocene-Oligocene boundary, when the oil pools had already been formed. Possibly these same processes governed the enrichment of the heavy oils in vanadium, nickel, and molybdenum. According to Colombo and Sironi (1961), the heavy oil and asphalt in these zones contains 55 to 248 g/t V and 30 to 155 g/t Ni, as well as an anomalously high concentration of Mo, as much as 171–183 g/t in the asphalt (Table 4.14). On the basis of the analytical relationship between [V], [Ni], [S], density, and the content of asphalt-resin substances in the petroleum and bitumens, we calculated the possible concentrations of metals in a whole group of heavy oil fields in Italy, for which we have no experimental data (Table 4.15).

It is interesting that in the southern part of the Apennines, the bitumens contain much less V (70–82 g/t), Ni (about 30 g/t), and Mo (1–2 g/t) than in the areas described above. This same abrupt change in concentrations of V and Ni is observed in the Sicilian basin, where the Gela and Nicosia deposits of ultra-heavy oil and bitumens contain about 150 g/t V and 90–95 g/t Ni, while such other fields as Ragusa and Siracusa are relatively rich in Ni (as much as 97.5 g/t) but have low concentrations of V (8–21 g/t). Such local variations in the rare and disseminated element composition of the petroleum probably are related to the conditions of their transformation in the pools.

The recoverable reserves of vanadium in the heavy oil pools of Italy can be estimated to be roughly 10,500 tons. Since these fields have been worked, about 3,300 tons of V and 3,600 tons of Ni have been recovered as by-products.

In the Cis-Dinaride depression in southeastern Albania, vanadium-bearing heavy oils in the Cuchevo and Patos Fields and bitumen in the Seleniza deposit are Miocene in age (Table 4.16). It has been suggested (Demenkova, 1956) that the vanadium and nickel in the petroleum and bitumen are

TABLE 4.14
Results of geochemical analyses of petroleum and natural bitumen from Italy [after Colombo and Sironi, 1961]

Field	Depth of occurrence (m)	Age	Density (g/cm^3)	Content (%)		Content (g/t)				Ratio	
				Sulfur	Total resins and asphaltenes	V	Ni	Mo	Cr	V/Ni	V/[A+R]
Central Apennines											
Allano	700	P_2^2K	0.9664	4.70	19.19	55.0	30.0	19.5	2.5	1.83	276
	1020	K	1.0912	8.73	55.71	229.0	106.0	90.5	10.1	2.16	411
Scafa	Surface	N_1	1.2768	9.84	61.85	248.0	109.0	82.0	9.1	2.27	400
Chelano	3000	K	1.2553	8.28	66.17	210.0	90.0	15.2	9.1	2.33	317
Casalbordino	1500	K	0.9953	4.91	23.05	95.0	57.5	3.2	3.1	1.65	249
Filettino	Surface	T	1.2736	11.37	76.12	196.0	154.0	171	1.2	1.27	257
Alatri	Surface	T	1.1279	8.21	71.35	229.0	155.0	183	10.0	1.47	320
Southern Apennines											
Baranello		P-N(?)	1.0398	5.23	50.69	82.5	29.7	1.0	5.0	2.77	162
Colle Sanita		P-N(?)	1.1101	5.51	62.59	73.0	32.7	2.0	1.0	2.23	116
Eastern Sicily											
Ragusa	Surface	N_1^2	1.0346	2.22	34.97	20.1	70.2	1.0	0.3	0.28	57
	Surface	P_3	1.0246	3.16	42.27	14.1	84.0	1.3	0.5	0.17	33
	1800	T_3	0.9380	2.40	33.73	8.1	41.0	0.8	0.1	0.20	24
Siracusa	2600	T_3	0.9882	3.95	37.51	21.5	97.5	2.6	1.0	0.22	57
Gela	3517	T_3	1.019	7.67	60.65	147	94.5	8.4	5.0	1.55	238
Nicosia	Surface	N	0.976	1.01	40.50	149	90.0	4.8	5.9	1.65	368

TABLE 4.15
Analytical and calculated concentrations of vanadium and nickel in heavy oil from Italy

Field	Density of petroleum		Concentration (g/t)			
	°API gravity	ρ_4^{20} (g/cm^3)	Analytical		Calculated	
			V	Ni	V	Ni
Dacion	21.8	0.9192	133	29	120	30
Pisticci-S. Cataldo	11.4	0.9868			140	90
Perla	13.3	0.9736			130	90
Gela	11.0	0.9926	147	94.5	145	92
Gela Mare	10.0	0.9966			150	95
Santa Maria	15.9	0.9599			120	85
Emilio	13.0	0.9726			130	90
Rospo Mare	11.0	0.9926			150	95
Sargo Mare	8.0	1.0110			165	97

primary, their source being Jurassic shales containing 2200–3000 g/t V and 300–660 g/t Ni in the organic matter. The genetic relationship of the vanadium-bearing crudes to these source rocks is confirmed by the high content of vanadyl porphyrins in the crude, reaching 1500 g/t in the petroleum and 1900 g/t in the bitumen.

Pannonian Province

The Pannonian oil and gas province is confined to an Alpine intermontane basin developed on a pre-Late Carboniferous central massif. As in the Adriatic basin, the pools of vanadiferous heavy oil (0.92–0.99 g/cm^3) are controlled by buried erosional highs of Triassic and Cretaceous carbonate rocks beneath a Neogene hiatus. These pools (Nagylengyel, Barabasszeg, and others) are situated in the West Bakony zone of oil and gas accumulation in Hungary.

The heavy oils contain 160 to 180 g/t V and 45 g/t Ni, with a sulfur concentration of 1.3 to 2.8 percent and, in the asphaltenes, 14–17 percent. It is noteworthy that the pools in the Pannonian sandstones overlying the hiatus (Lovaszi, Budafanuszta, and others) have a density of 0.82–0.88 g/cm^3 and are practically devoid of V (0.03–0.1 g/t). This confirms the view expressed above concerning the paleo-supergene nature of these heavy, vanadiferous oils.

Among the other oil and gas basins of Western Europe, fields containing heavy oil are known in the Central European Basin: Hellm, Helder, Berkel, Zoetermeer, Sjonebek, and others in the Netherlands; Heide, Itzel, Nordhorn, and Steinbek in Germany; the Lacq, Lugo, Castera Louis Mimizan Fields, and others, in the Aquitanian Basin of France; and the Amposta Marina, Dorada, and other fields of the Algiers-Provence Basin in Spain. Available analytical data indicate that most of the heavy oils contain low concentrations of vanadium (up to 20–40 g/t) and nickel (up to 10–20 g/t), even when the sulfur content in individual pools is high (up to 4.3 percent). On the whole, however, the heavy oils have a relatively low sulfur content (up to 1.0 percent) and a not very high content of asphaltene components.

TABLE 4.16

Physicochemical and trace element composition of heavy oil and natural bitumen from Albania [after Demenkova, 1956]

Field	Depth of occurrence (m)	Age	Density (g/cm^3)	Sulfur (%)	Resins + asphaltenes (%)	V (g/t)	Ni (g/t)	VO-p (g)	V/Ni	V/[A+R]
Kuchova	500–600	N_1	0.9684	4.11	27.63	168.1	33.9	976	4.95	610
Pahtos	20–1265	N_1	0.9916	5.41	36.40	284.5	64.0	1588	4.44	770
		N_1	1.0180	6.15	48.84	554	117		4.73	1130
Selenitza		N_1	asphalt	7.78	62.60	521	161.3	1942	3.23	830
Fieri		J_2–K_1	vein asphaltite	6.03	86.50	1650	320		5.15	1800

Only isolated deposits of heavy oil in the Ebro Basin and Algiers-Provence Basin in Spain could be of definite interest with respect to vanadium potential.

4.5 NEAR AND MIDDLE EAST

Persian Gulf Province

The Persian Gulf oil and gas basin is located in the junction zone between the African-Arabian platform and the Alpine fold belt (Figure 4.24). About 300 oil and gas fields have been found in the basin, with proven petroleum reserves of more than 60 billion tons. Miocene, Paleogene, Cretaceous, Jurassic, Triassic, and Permian reservoirs, chiefly carbonate, are oil- and gas-bearing. Within the province, about 40 fields with pools of heavy oil (less than 19°API) have been found: 13 in Turkey in the Lower and Upper Cretaceous; six in Syria in the Lower-Middle Miocene and Upper Cretaceous ("Massive limestone"); seven in Iraq in the Miocene and Upper Cretaceous; five in Saudi Arabia in the Lower-Upper Cretaceous Burgan Formation and the Upper Jurassic; and three in Oman in the Lower Cretaceous. All the heavy oils have a relatively high sulfur content of 3.5–7.3 percent.

The relationships between V and [Ni], [S], and density that we calculated for the Paleogene and Cretaceous oils, on the basis of published (Vysotskiy and Guseva, 1977) and new analytical data, showed that there is a linear relationship between the two oils, typical of primary vanadiferous petroleum in the course of petroleum formation (Figure 4.25). The high content of primary vanadium may be evidence of the presence of oil-bearing metalliferous domanikoid formations.

Paleogene petroleum

(26) $[V] = 888.9 \cdot \rho - 728.9$

(27) $[V] = 1.2 \cdot [Ni] + 12.0$

(28) $[V] = 20.0 \cdot S$

Cretaceous petroleum

(29) $[V] = 1071.4 \cdot \rho - 891.4$

(30) $[V] = 3.18 \cdot [Ni]$

(31) $[V] = 29.8 \cdot [S]\ 32.8$

These relationships enabled us to calculate the concentration of vanadium and nickel in heavy oil fields for which we had no experimental data (Table 4.17).

This table shows that the concentration of vanadium in the heavy oils is relatively low, the values falling at the level typical of primarily-vanadiferous heavy oils of the supergene-residual subtype. For petroleum with 9–16°API density (1.0037–0.9556 g/cm^3), the vanadium concentration in the Paleogene petroleum is 120–163 g/t and in the Cretaceous, 132–184 g/t; for a density of 16–25°API,

FIGURE 4.24

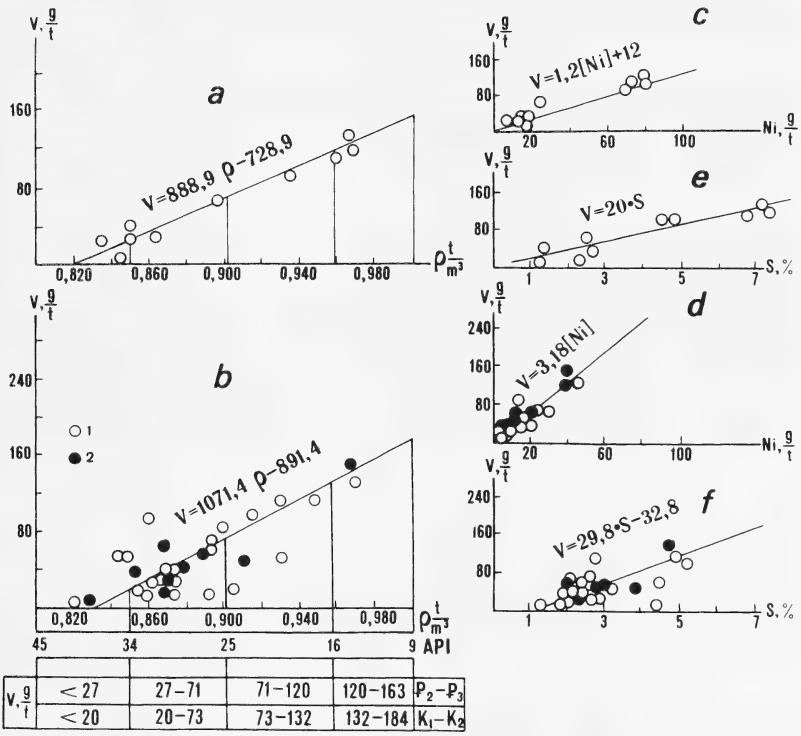
Location of heavy oil fields in the Persian Gulf Basin

1 – Heavy oil fields

2 – Heavy oil fields with high concentration of vanadium

3 – Zones of distribution of heavy oil fields

4 – Boundaries of oil basins



V, g/t	< 27	27–71	71–120	120–163	P_2–P_3
	< 20	20–73	73–132	132–184	K_1–K_2

FIGURE 4.25

Calculated average concentration of vanadium in the Persian Gulf Basin as a function of density of: Eocene-Oligocene (a) and Cretaceous (b) oil; nickel, in P_2–P_3 (c) and K_1–K_2 (d) oil; and sulfur, in P_2–P_3 (e) and K_1–K_2 (f) oil

1 – K_2

2 – K_1

TABLE 4.17
Analytical and calculated concentrations of vanadium and nickel in the heavy oil from the Persian Gulf Basin

Elements	Density of oil		Concentration (g/t)			
	°API gravity	ρ_4^{20} (g/cm^3)	Analytical		Calculated	
			V	Ni	V	Ni
Turkey						
Dacion	21.8	0.9192	133	29	120	30
Raman	18.7	0.9383			90–110	37
Bati Raman	13.3	0.9736			130–150	40–48
Germik	18.8	0.9377			90–105	30
Magrip	18.4	0.9402			100–115	35–40
Sezgin	17.0	0.9492			115–130	40
Camurlu	12.2	0.9846			125–150	40–50
Iliztepe	11.3	0.9908			130–170	42–53
Guney Dincer	16.7	0.9510			115–127	35–40
W. Cozluca	12.0	0.9826			120–160	40–50
S. Sinan	13.0	0.9726			130–150	40–48
Kahta	11.0	0.9926			135–172	43–54
Syria						
Alian	19.0	0.9365			100–110	35
Kbeibeh	18.0	0.9428			105	75
Tichrin	18.0	0.9428			105	75
Jbesseh	18.0	0.9428–0.934	97	70	85–100	60–80
Sfayeh	14.4–17.5	0.967–0.9497	439–521			
Iraq						
East Baghdad	17–23	09492–0.9120			85–125	26–40
Dujaila	13.0–16.0	0.97–0.95			110–145	
	12.0–17.5	0.98–0.94			120–165	37–50
Awasil	9.5	1.000			180	56
Qaiyarah	16.0	9.5556			120	
Iran						
Cyrus	18.3	0.9408–0.967	151	39	145	45
Darius	21.9	0.9186			90–100	
Qarn Alam	14.8	0.9635			140	45
Habur	14.8	0.9635			140	45
Mukhaizna	15.0	0.9623			130	40
Jalmud	21.0	0.9241			100	30

these values will be 71–120 g/t and 73–132 g/t, respectively. In the light oils, with a density greater than 34°API (0.8508 g/cm^3), the vanadium concentration should not exceed 20 g/t in the Cretaceous petroleum and 27 g/t in the Paleogene. These levels of accumulation of vanadium in petroleum are typical of basins in which the petroleum was generated with catagenesis stages not higher than MK_2 (MK_1–MK_2) and source rocks in which sapropel-type organic matter was dominant.

According to our determinations, vanadium concentrations that are anomalous for the province were found in the Upper Cretaceous heavy oils in the Sfayeh Field (Syria), where, in petroleum with a density of 0.944 to 0.967 g/cm^3, the vanadium content is 439 to 521 g/t. Probably this enrichment in V is related to secondary processes.

Considering that most heavy oil fields in the Persian Gulf Basin are being developed, vanadium is recovered as a by-product with the petroleum. Calculations show that in the heavy oil fields of Turkey alone, on the order of 2,000 tons of vanadium have been extracted, and probably lost, since the beginning of exploitation.

Together with V and Ni, the petroleum of this province contains relatively high concentrations of Ag, Cd, Cr, Zn, Pb, and other elements (Ali, Bukhari, and Saleem, 1983). In some crude oil of Saudi Arabia, the Ag content reaches 0.31–0.39 g/t (Fadili and Abqaiq Fields) and that of Cd, 1.7–2.3 g/t (Abu Safah and Safaniyah Fields). With petroleum reserves of 1620 million tons in the Abqaiq Field, it is postulated to contain 630 tons of silver; in the Safaniyah Field, with petroleum reserves of 3160 million tons, the amount of cadmium in the oil is calculated to be 7500 tons.

In refining Middle East petroleum, the possibility of concentrating, for industrial use, valuable by-product components of V, Ni, Ag, *etc.* in the heavy residues, especially in the coke and ash, must be considered.

4.6 AFRICA

The metal potential of the heavy oil and bitumen on the African continent have hardly been studied despite the existence of large accumulations in Nigeria and Zaire, on Madagascar, and in other areas (Meyer and de Witt, 1990).

Among the oil and gas basins of North Africa, the main high-sulfur heavy oil resources are related to the Gulf of Suez rift basin, which is part of the epi-cratonic orogen system of East Africa. The producing formations in the Gulf of Suez basin occur over a wide interval in the section, from Devonian to Miocene in age, with heavy sulphurous and high-sulfur (1.7–4.7 percent) petroleum in Paleozoic, Cretaceous, and Eocene fields and heavy, high-sulfur and sulfurous, paraffin-based petroleum in the Miocene fields, which contain the main reserves. According to available analytical data (Vysotskiy and Guseva, 1977), the petroleum has a relatively high content of vanadium (from 48.9 to 135.9 g/t) and nickel (from 18 to 71.9 g/t). The relationships that we calculated, on the basis of these data, between the vanadium content and density and the sulfur and asphaltene content of the petroleum (Figures 4.26 and 4.27; Table 4.18) showed that there is a linear relationship between them, of the following form:

(32) $[V] = 907.69 \cdot \rho - 771.54$

(33) $[V] = 36.33 \cdot S - 8.33$

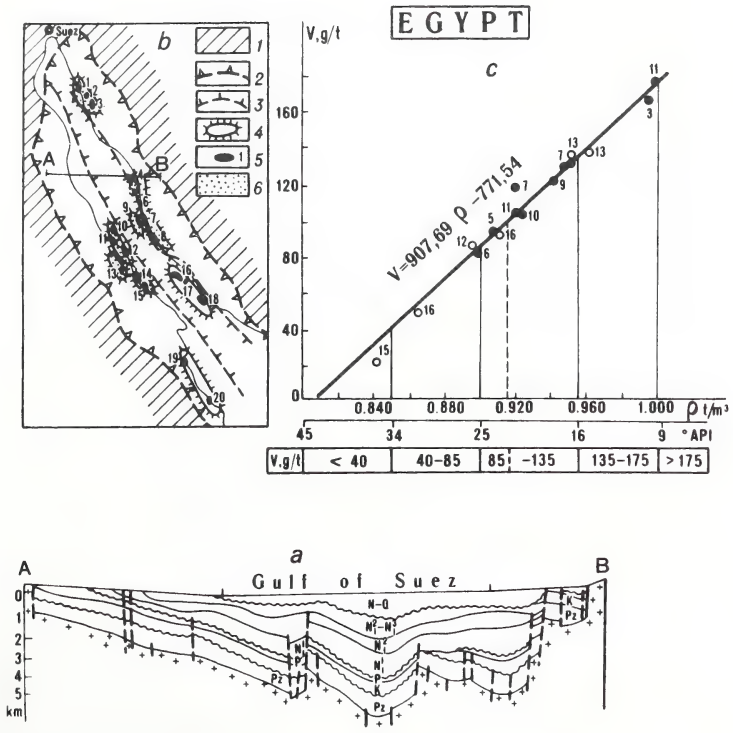


FIGURE 4.26

Geologic cross section A–B (a), map of zones of accumulation of vanadiferous petroleum (b), and diagram of vanadium concentration as a function of density (c) in fields in the Gulf of Suez Basin, Egypt

1 – Exterior basin area
2 – Basin margins
3 – Principal faults
4 – Zones of oil accumulation
5 – Oil fields
1. Sudr
2. Matarma
3. Asl
4. Abu Rudis
5. Sidri
6. Vadi–Feran
7. Belayim Land
8. Abu Durba
9. Belayim–Marine
10. Ras Amer
11. Ras Bakr
12. Ras Garib
13. Karim
14. Um Jsr
15. Shukeir
16. El Morgan
17. Amal
18. Ras Garaa
19. Gemza
20. Harghada

6 – Vanadiferous petroleum zones

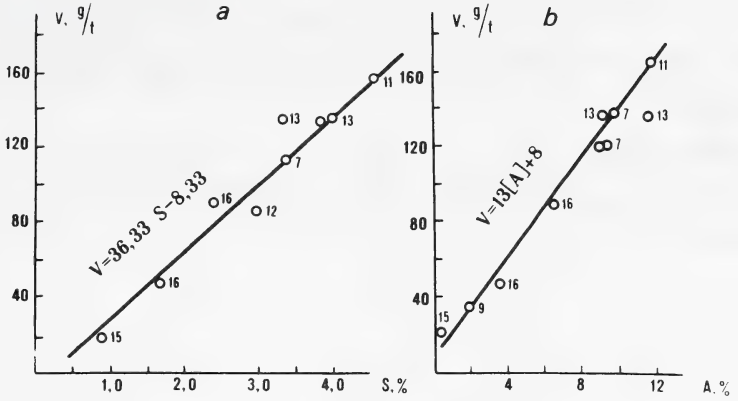


FIGURE 4.27
Vanadium concentration as a function of sulfur (a) and asphaltene (b) content of oil in selected fields of the Gulf of Suez Basin

TABLE 4.18
Density, percentage of asphaltene and sulfur, and vanadium pentoxide resources in selected fields from the Gulf of Suez

Oil field	Age	Depth (m)	ρ_4^{20}	A (%)	S (%)	V_2O_5 resources (10^3 t)	Estimated resources of V (g/t)
Belayim	N_1^2	1556–1582	0.952	12.0	2.12		130
	N_1^2	2526–2591	0.927	9.1	3.30	12.0	115
Belayim-Marin	N_1^2	2094–2124	0.945	12.1	3.51		125
Ras Bakr	N_1^2	7000–1250	0.918	8.5	4.11	3.0	110
	K_2		0.926	9.4	4.03		110–135
	C_1		0.965	11.5	4.60		145–165
	D_1		1.013	12.3	3.87		175
Ras Sudr	N_1^1	685–693	0.951	–	2.3	1.5	120
	P_2	830–840	0.938	–	2.0		110
ASL	N_1^1	1109–1168	0.920	5.6	1.84	1.0	100
	P_2	927–1028	0.920	5.7	1.89		100

(34) $[V] = 13.00\,[A] + 8$

For heavy oils with a density of 9 to 16°API (1.0037–0.9556 g/cm^3), the vanadium content should fall within the range of 135–175 g/t, with a sulfur content of more than 3.5 percent and an asphaltene content of more than 9.0 percent. Such parameters are typical of primarily vanadiferous petroleum, generated by source rocks with sapropel-type organic matter in stages of catagenesis not higher than MK_2.

Considering the large resources of vanadiferous heavy oil in the Gulf of Suez basin, it can be profitable to recover the vanadium during refining. According to our calculations, the losses during development of such fields already have amounted to at least 20,500 tons of vanadium, and 11,700 tons of nickel.

5

RARE ELEMENTS IN OIL (BLACK) SHALES

5.1 ACCUMULATION AND COMPOSITION OF THE SHALES

In the Phanerozoic section, a fairly distinct periodicity has been found in the accumulation of the sapropelic carbonaceous rock facies termed oil shales, black shales, domanikites, and the like. Many of these are enriched in Mo, U, Re, V, Se, Cd, Bi, Tl, Ag, Au, As, Sb, and other rare and disseminated elements. Against a relatively high overall geochemical background in carbonaceous rocks, groups of formations are distinguished which are characterized by a certain combination of rare elements. The content of the elements is several orders of magnitude higher than their clarkes and may reach the levels of economic ore concentrations. On the basis of current ideas concerning the concentrating function of organic matter, sapropelic carbonaceous formations as a source of metals should reflect the conditions of accumulation and fossilization of the organic matter and the environment of deposition. The difference in the environments in which black shales of different genetic types are formed is manifested not only in the distribution and concentration of rare and disseminated elements, but also in the mineral composition of the rocks, which enables us to correlate their composition and metal potential. A proposed compositional classification (Goldberg, Mitskevich, and Lebedeva, 1991) was based on a combination of methods, including X-ray, silicate and carbonate-chemical, and petrographic, with the chemical methods of principal importance. The chemical analyses were recalculated to the complete mineral composition, bringing out the main components of these rocks: free authigenic silica; carbonates; and clastic components, which consist mainly of clay minerals. On the basis of processing about 500 analyses of black shales from various basins with respect to these components, five types of rocks were distinguished. The first three types — siliceous, clayey-siliceous, and siliceous-carbonate — can be classified as sediments of the domanik type on the basis of the details of their formation, distribution, and composition. These rocks always contain an elevated, often high, amount of free authigenic silica which most investigators believe to be planktonogenic. Domanikites are the sediments of uncompensated ("starved"), relatively deep-sea basins, accumulated at an extremely low rate (up to 6 m/Ma) with an oxygen deficit in the bottom water and extensive hydrogen sulfide contamination. The decisive factors in the accumulation of organic matter in these sediments are the low sedimentation rates, with very slight inorganic dilution, and a high degree of fossilization of organic matter, mainly due to the formation of organo-montmorillonite compounds. At the same time, these factors promoted long-term processes of absorption of the metals by active organic matter from the sea water during early diagenesis, which led to the formation of strong geochemical anomalies. It is well known that functional groups with coordination saturation of oxygen and nitrogen atoms rise to the surface of organic matter and take part in binding metals in compounds of the chelate type.

Another variety of carbonaceous deposit is oil shale proper, which is composed of clastic and clay-carbonate rocks practically devoid of authigenic silica. Most of the richest oil shale deposits, containing up to 20–50 percent organic matter, are related to these. The main factor controlling the accumulation of large masses of organic matter apparently was the abruptly increased primary bio-productivity (the P factor of Yudovich and Ketris, 1988).

Because oil shales, as a rule, were formed in shallow marine or continental basins, the accumulation and preservation of organic matter is guaranteed only if the sedimentation rate is high, leading to rapid burial of the sediment. In addition, a considerable amount of organic matter (including humic) was introduced with the clastic material, as is indicated, particularly, by the presence of highly carbonaceous rocks in the purely clastic sections of intermontane basins. It is noteworthy that, in contrast to domanikites, the predominant clay minerals of oil shales proper are hydromicas and

kaolinite, which do not form organomineralic compounds and do not preserve organic matter. The separation of organic matter from the inorganic components of oil shales determines their distinctive qualitative parameters: the output of shale resin and the heating capacity. In addition, the specifics of the formation of oil shales did not foster the concentration of these elements in oil shales. These factors include a high sedimentation rate, a brief period of diagenesis and rapid separation of the sediment from the bottom water layer, and, frequently, accumulation in closed freshwater bodies which were impoverished in rare elements in the aqueous environment.

Table 5.1 summarizes the most important indices for distinguishing the environment of formation as well as the mineralogic, lithologic, and geochemical characteristics of domanikites and oil shales proper.

5.2 ORE SPECIALIZATION OF THE SHALES

The classification of domanikite and oil shale facies that has been worked out on the basis of composition and genetic criteria is tied in with the distribution of included rare and disseminated elements.

The material on which these formulations were based includes numerous data on the trace element composition of black shales published in our own and in the foreign literature, as well as results of analytical investigations of shales made by neutron activation, X-ray fluorescence, and emission spectral analyses. The various basins studied include, among others, the Baltic, West Siberian, Olenek, Timan-Pechora, Volga, and Central Asian.

In dealing with the problems of classification, most attention has been paid to study of the patterns of distribution of rare elements in carbonaceous facies of various types as the basis for the prediction of their metal potential. On the basis of calculations made for the concentrations of a number of elements in black shales, we were able to ascertain the nature of the association of organophilic elements and, on that basis, to classify the principal Phanerozoic carbonaceous facies of the world. These metallogenic facies were determined on the basis of a series of elements that had stable maximum values of concentration coefficients (C_c) for the type of facies in question: the ratio of the elemental content of a rock enriched in organic matter (≥ 5 wt%) to its clarke for clays. In addition, the next series of elements which considerably exceeds the clarke level was taken into account in the classification In some black shale facies, secondary mineralization has been superposed on the primary geochemical background of the facies. This is related to the introduction and deposition of metals at geochemical barriers, as a rule in mineral form. In addition, in zones of old upwelling, strong geochemical anomalies appear, mainly in P, U, and V, which blur the main series of rare and disseminated elements accompanying the planktonogenic sapropelic organic matter of black shales.

Table 5.2 gives the main metallogenic types of domanikite and oil shale that have been distinguished, and the concentration coefficients of elements defining these types. The combination of elements accompanying sapropelic organic matter in domanikites on the one hand, and in oil shales on the other, remains fairly constant. In the various associations, mainly domanikite, only redistribution of the elements in the concentration order is observed, with the formation of typical metallogenic associations of a relatively small number of elements (Mo, Re, U, Se, V, Zn, Cd, Bi, Ag, Tl, and others).

TABLE 5.1
Comparative characteristics of oil shales and domanikites

Indicators	Oil shales	Domanikites
Regime of deposition/rate of deposition (m/Ma)	Compensated, relatively high, up to 50–100	Uncompensated low, up to 1–6
Facies setting	Shallow sea, lagoons, lakes	Relatively deep sea (up to 500–1000 m); extensive hydrogen sulfide contamination of water above bottom
Tectonic setting	Intraplatform syneclises, shallow depressions on platform structures, intermontane basins	Platforms, chiefly regions of pericratonic subsidence; geosynclinal regions
Area of occurrence (km^2)	Isolated basins, tens to hundreds, rarely thousands	Continuous over areas of tens to hundreds of thousands to a few million
Host rocks	Sandstones, siltstones, conglomerates, effusives, clayey rocks, rarely carbonates; coal is found	Clayey and clay-carbonate rocks, limestones
Type of rocks enriched in organic matter	Clayey and carbonate-clayey oil shales, usually silty	Siliceous, clayey-siliceous, clayey and siliceous-carbonate domanikites
Rock-forming minerals	Hydromicas, kaolinite, montmorillonite, calcite, dolomite, pyrite; considerable silt admixture	Montmorillonite, calcite, dolomite, opal, chalcedony, pyrite; slight admixture of silt
Thickness of sequence containing rocks rich in organic matter (m)	Hundreds, sometimes a few thousand	A few tens
Number of intercalations (beds) rich in organic matter	Tens	Isolated; one or two economically ore-bearing
Amount of organic matter at end of diagenesis (%)	15–50	5–20, rarely up to 35
Type of organic matter	Humite-sapropelite, sapropelite	Mainly sapropelite
Heating capacity (Kcal/kg)	1000–4500 (usually 2000–2500)	800–2500 (usually about 1000)
Yield of shale tars (%)	3.5–32.5 (usually 10–15)	1.5–8 (usually 3–4)
Content of elements	About clarke; above clarke: Mo, Re, sometimes P, U, Se, Cd, Au, Ag, As, Cu	Everywhere 1–4 orders above clarke: Re, Mo, Se, Cd, Bi, Ag, Au, As, Tl, Sb, U, V, Zn; often P, Ni; sometimes Cu, Pb, Co, Cr

Among domanikites of clayey-siliceous (siliceous-clayey) composition, two main metallogenic types are distinguished: Mo-U-V (Re, Bi) and Mo-Se-Zn (Table 5.2).

Classic examples of the first metallogenic type are the Cambrian Alum Shale and Ordovician Dictyonema shales, underlying the territory from northern Norway to southern Sweden. The accumulation of the Alum shales corresponded to the stage of maximum transgression with minimal sedimentation rates (1 to 2 m per Ma). In the stratigraphic section of the Alum shales, which is from 1219 m (Nyarke) to 50 m thick (Skane), three members with different contents of organic matter, sulfur, and metals are distinguished. A general tendency is observed toward an increase in concentration of C_{org}, S, U, Mo, and Ni upward in the section. Numerous inclusions of concentrated organic matter (up to 80 percent), the so-called "kolms," containing up to 10 percent FeS_2 and 2000–5000 g/t U, are confined to the Peltura zone of the upper Renstad member (Andersson *et al.*, 1985); the background concentrations are 15–30 percent C_{org}, 135–337 g/t U, and 240–340 g/t Mo. In the Tremadocian Dictyonema shales, a very high concentration of V is observed, despite a decrease in the organic matter content to 68 percent.

On the basis of concentration coefficients, the disseminated and rare elements in shales form the following series (the first figure is the minimum C_c value, the second, the maximum): Mo (35–230), U (4.5–105), V (3.4–28), As (2.5–24), Cd (7.3–23), Ag (3–14), (Sb 3–10), Zn (1.6–3.3), and Cu (1.3–3.3); in individual samples, Bi (130) and Pb (46) have been found. A fairly clear relationship of the shales richest in rare and disseminated elements, especially U and Mo, to the zones with minimum thickness of the shale-bearing member is found. It is to these zones that the shale deposits of Sweden, containing large reserves of U, Mo, and other elements, are confined (the Nyarke, Billingen-Falbigden, Renstad, and Ostergotland). For instance, the uranium reserves in the Billingen-Falbigden deposit are estimated at 1.7 million tons and those of the Nyarke deposit, 0.28 million tons (Andersson *et al.*, 1985). The source of the uranium in the shales is believed to be the weathered mantles overlying basement granites of the Baltic shield, as well as associated deposits of the uranium-albite association (Yudovich and Ketris, 1988). In addition, the strict stratification of the uranium mineralization throughout the section and its areal persistence may indicate biogenic accumulation of uranium, if its concentration in the paleo-basin is relatively high.

The kerogen mudstones of the Tremadocian Tyurisalus formation in northern Estonia may be an analog of the Dictyonema shales of Scandinavia. According to Pukkkonen (1989), the order of decreasing average values of rare and disseminated element concentration coefficients in shales is as follows: Re (143), Bi (111), Mo (69), U (15), Tl (10), Ag (10), Au (10), Cd (9.5), V (7), Sb (7), As (5), Se (5), and Cu (2.5). In some sections a high concentration of Zn (up to 7100 g/t) is observed. With the decreasing thickness of the shale layer from west to east and toward the south, from 7 to 1 m, there is an increase in the concentration of Re, V, Mo, U, P, S, Ag, As, and Ni and a decrease in the content of C_{org}, Nb, Al, and others. For instance, from the central part of northern Estonia to the Toolse deposit, the V content increases from 760 to 1040 g/t, Mo from 133 to 406 g/t, and Re from 0.05 to 0.17 g/t (Maremäe, 1989).

Black shales such as the Chattanooga (Hathaway member), which extends parallel to the Appalachians from New York to northern Texas, belong to the first metallogenic type. The Chattanooga shales were deposited in a vast (more than 650,000 km^2), relatively deep, stagnant epicontinental basin with extremely slow sedimentation rates. Conant and Swanson (1961) pointed out the similarity of the Chattanooga shales to the Alum shales of Scandinavia, with respect to their conditions of formation and composition. Analysis of data on the trace-element composition also

TABLE 5.2
Metallogenic types of domanikite and oil shale associations

Basin	Country	Age of horizon, formation	Type of association	Predominant rock composition	Organic matter, range/average (%)	Metallogenic associations (in order of decreasing C_o)		Elements forming their own minerals	Examples of deposits (metal content, g/t)	Reference
						Main	Secondary			
Type I. Mo-U-V (Re, Bi)										
Baltic	Sweden	O_1, Dictyonema	Domanikite	Siliceous-clayey	6–15/–	(Bi), Mo, U, V	As, Au, Ag, Zn, Cu	Fe	Ostergotland (Mo-135; U-140–190; V-2000)	
		ϵ_2–ϵ_3 "alum shales"	Domanikite	Siliceous-clayey	5–30/12	(Bi), Mo, U, V	As, Ag, Au, Cd, Zn, Cu	P, Fe	Nyarke (Mo-270; U-135–245 V-1000); Billingen-Falbigden (Mo-270–340; U-155–337; V-780)	Andersson and others (1985); Anderson and Bjerle (1988)
	Estonia	O_1, Pakerort, Tyurisalu	Domanikite	Siliceous-clayey	5–14/11	Re, Bi Mo, U, V	Au, Ag, Cd, Sb, As, Se	P, Pb, Zn, Fe	Toolse (V-1040; Mo-406; Re-0.17)	Pukkonen (1989); Märemäe (1989); author's data
Chattanooga	USA	D_3–C_1^1	Domanikite	Siliceous-clayey	5–25/22	Mo, U, V	Ag, Zn, Cu, Th	P, Fe (Mo-100;	Chattanooga (Mo-100; U-80–120; V-500; (Mo-200; V-1500)	Conant and Swanson (1961); Landis (1962); Vine (1964)
Type I. Mo-U-V (Re, Bi)										
Illinois	USA	C_2–C_3	Domanikite	Siliceous-carbonate	4–24/–	P, U, V, Mo, Se, Zn	Cu, Ni, Pb, Cd	P, Pb, Mo Zn, Fe	Logan Quarry (P_2O_5-1%; U-240; V-1430; Se-300); Mecca Quarry (U-160; V-5850; Mo-1160; Se-250)	Davidson and Lakin (1961); Coveney and Martin (1983)

Table 5.2 cont'd ...

Basin	Country	Age of horizon, formation	Type of association	Predominant rock composition	Organic matter, range/average (%)	Metallogenic associations (in order of decreasing C_c) Main	Secondary	Elements forming their own minerals	Examples of deposits (metal content, g/t)	Reference
Type II. Mo-Se-Zn										
West Siberian	Russia	J_3v-K_1v, Bazhenovo	Domanikite	Siliceous-clayey	6–15/10	Mo, Se, Zn, U, As, Sb	Au, Ag, V, Ni, Cu	Fe	–	Gavshin and Bobrov (1982); Gurari and others (1988); author's data
Type III. U										
California (Ventura Los Angeles)	USA	N_1, Monterey, Sisquoc	Domanikite	Siliceous & clayey siliceous	4–14/5.4	U	Mo, Cr, Be, Y V, Cu, Ni	P	Temblor Range (U-240)	Durham (1987)
Type IV. P-U-V (Mo, Se, Zn)										
Phosphoria (old upwelling zone)	USA	P_1, Phosphoria (Meade Peak horizon) "vanadium zone"	Domanikite	Siliceous-carbonate	7–10/5	P, V, U, Mo, Se, Zn	Ni, Cu, Cd, Pb	P, Zn, Pb, Fe	(P_2O_5-30.5%; U-120; V-500–4000 Se-680; Mo-500; Zn-3500)	Love (1961); Sheldon (1959);
Type V. Mo-V (Cd, Bi, Ag)										
Olenek	Russia	ϵ_1–ϵ_2 Kuonamka	Domanikite	Siliceous-carbonate	6–33/14	Mo, V, Ag Bi, Cd	Zn, Au, Se As, Sb, Ni	P, Fe	–	Bakhturov, Yevtushenko and Pereladov (1988); Gavshin & others (1984); author's data
Eromanga	Australia	K_1, Tooleback	Domanikite	Siliceous-carbonate	4–26/13	Mo, Bi, Cd Se, V	Zn, U, Ni As, Ag, Sb	Fe	Julia Creek (Mo-270; V-2000; Cd-25; Se-30; Au-5; U-30)	Glikson and others (1985); Patterson & others (1985); Riley and Saxby (1982)

Table 5.2 cont'd ...

Basin	Country	Age of horizon, formation	Type of association	Predominant rock composition	Organic matter, range/average (%)	Metallogenic associations (in order of decreasing C_c) Main	Secondary	Elements forming their own minerals	Examples of deposits (metal content, g/t)	Reference
Type VI. Ag-Mo-Zn (Cd, Bi, Tl)										
Atlantic Ocean		K	Domanikite	Siliceous-carbonate	–/(6)	Bi, Cd, Tl, Ag Mo, Zn, V	Cu, Cr, Ni, Co	Fe	–	Brumsack (1980); Brumsack and Lew (1982)
Type VII. Re-Mo-Se (Cu, Zn, Pb, Ag)										
Edinburgh	Great Britiin	P_2 Merle Slate	Domanikite	Siliceous	4–11/–	Re, Mo	Ag, V, Ni, Cu, Co	Fe	Merle Slate (Re-0.1–30; Mo-20–800)	
Central European	Germany	P_2, Kupferschiefer "Copper schists"	Domanikite	Siliceous	7–15/–	Cu, Zn, Pb Ag, Re, Se, Mo	Au, As, V, Ni Co, Cd, Ge, U	Cu, Pb, Zn (Cd), Ag, Fe	Mansfeld (Cu-2.5%; Zn-0.7%; Pb-0.44%; Re-0.7%; Se-300; Mo-65–920); Sangerhausen (Cu-2.95%; Zn-1.25%; Pb-0.64%; Ag-106; Re-21; Mo-201)	Wedpohl (1967); Lur'ye (1983)
	Germany	P_2 Kupferschiefer	Domanikite	Siliceous	7–15/–	Cu, Zn, Pb Ag, Re, Se, Mo	Au, As, V, Ni Co, Cd, Ge, U	Cu, Pb, Zn (Cd), Ag, Fe	Richelsdorf (Cu-1–3%; Zn-0.6–1.0% Pb-0.5–0.7%)	
	Poland	P_2 Kupferschiefer	Domanikite	Siliceous	10–13/–	Cu, Zn, Pb Ag, Se, Re, Mo, Au, Pt, Pd	Au, V, Ni Bi, Ir, Os	Cu, Pb, Zn Ag, Fe	Lubin-Serouzovice (Cu-4.5%); Zechstein (Se-300; Mo-80–310)	Kucha (1985)
Syr Dar'ya Upper Amur	Tadzhikistan, Uzbekistan	P_2 Suzak	Domanikite	Siliceous-carbonate	12–31/–	Re, Mo, Se, Cd	Tl, Bi, V, Ag Ni, Sb, Cu, Zn	Fe, P	Baysun (Mo-1500; (Mo-1500; V-1262; Se-78; Re-5.6; Tl-6.3; P-5250); Urtabulak (Mo-1500; Re-6.2)	Kler and others (1987); Poplavko and others (1977);

Table 5.2 cont'd ...

Basin	Country	Age of horizon, formation	Type of association	Predominant rock composition	Organic matter, range/average (%)	Metallogenic associations (in order of decreasing C_c)		Elements forming their own minerals	Examples of deposits (metal content, g/t)	Reference
						Main	Secondary			
Type VIII. Re-Mo										
Volga and Timan-Pechora	Russia	J_3v_1,	Oil shale	Clayey-carbonate	7–15/– 15–40/–	Re, Mo	Se, Cd, Bi, Au Ag, As, V, Ni, Sb, Zn, Tl	Fe	Kashpir; Ayyuva, etc.	Kler and others (1987); author's data
Type IX. Mo										
West European	G. Britain Spain, France Germany Switzerland and others	J_1, "Posidonia shales"	Oil shale	Clayey-carbonate	10–30/–	Mo	V, Ni, Co, Cu, Cr	Fe, (Li), Sr	Stowell Peak (Mo-60); Corset (Mo-15–260); Wurtenberg (Mo-80); Mont Terri (Mo-40)	Bitterli (1960); Kunz and Bauss (1975); Tourtelot (1970)
Picesance Creek Green River, Uinta, Washiki	USA	P_2, Green River	Oil shale	Clayey-carbonate	8–50/14	Mo,P, U	As, Zn, Cu V, Au	Na, Ba, Sr Fe, P, U	Wilkins Peak (Mo-200); (Mo-30); P_2O_5-2.2–18% U-0.005–15%	Yudovich & Ketris (1988); Meddaugh & Salotti (1983); Saelher *et al.* (1984); Saether, Runnells, & Meglen (1984)

indicates that the content of rare and disseminated elements in these facies is of much the same type (Landis, 1962; Vine, 1964). According to data on the concentration coefficients, the principal elements in the Hathaway shales form the following series (minimum and maximum C_c): Mo (50–115), U (25.0–37.5), V (4.0–11.5), Ag (2–20), and Zn (2–11). In Tennessee alone, the in-place uranium reserves in the shales are estimated to be 4.2–5.1 million tons.

The unique conditions under which the metals accumulated in the black shales are observed in the Illinois basin, where maximum concentrations of Mo, U, V, Se, and Zn are confined to shales that were deposited on the eastern littoral zone of the basin, near the old shoreline, at the boundary between reducing and oxidizing environments (Davidson and Lakin, 1961). This single region of concentration at a geochemical barrier occupies an area of several thousand square kilometers in Indiana and Illinois, in which rare and disseminated elements form the following series with respect to C_c values (minimum and maximum C_c): Mo (360–580), Se (400–500), Zn (37–111), U (50–75), V (11–45), and so on. Coveney and Charon (1983) found that Mo in the shales is bound mainly in organic matter, V in hydromicas, and U in organic matter and phosphates, whereas Zn, Cd, Cu, Pb, and, in part, Mo are in mineral form and consist of sphalerite, chalcopyrite, covellite, molybdenite, and other sulfides.

The second metallogenic type is typical of the siliceous-shaly Volgian-Valanginian domanikites (Bazhenovo formation) of the West Siberian Basin, with stable anomalous concentrations of Mo, Se, Zn, As, Sb, and other rare and disseminated elements (Table 5.2). The bituminous mudstones (20–35 m thick) accumulated in a vast (0.8–1.0 million km^2), relatively deep, uncompensated marine basin under conditions of widespread hydrogen sulfide contamination of the bottom water (Gurari, Vayts, Moskvin *et al.*, 1988). The average organic matter content in the rocks of the Bazhenovo formation is eight percent, reaching 12–15 percent in the central part of the basin. According to Gavshin and Bobrov (1982), the elements that accumulated in the organic matter are, in descending order of average values of concentration coefficients: Mo (61), U (10.5), As (7.3), Sb (6.9), Zn (5.9), V (4.6), Ni (4.1), Au (4.0), Ag (3.9), Cu (3.3), and Ba (2.8). An increase in concentration of organophilic elements from the periphery to the center of the basin is observed, with maximum values in the Salym, Surgut, and Krasnolininsk areas. According to the results of our activation analyses, the average rare and disseminated element concentration coefficients in the bituminous mudstones of the Salym area have the following values: Se (170), Mo (104), Au (25), Zn (17.5), As (16), Ag (14), V (8), Sb (5), Ni (4), and Co (2).

The main reason for the relative enrichment in rare earths of the rocks of the Bazhenovo Formation probably was the very slight mineral dilution due to the extremely low sedimentation rates. This conclusion is deduced particularly from the observed relationship between the rare and disseminated element concentrations and the ratio between the contents of organic matter and clay minerals in the rocks. From the clayey-siliceous rocks of the Bol'shoy Salym area to the siliceous-clayey rocks in the eastern part of the Shirotnoye Priob'ye ["Latitudinal Ob'"] area, to the clayey domanikites of the Nadym and Tazovsk areas, as the ratio of organic matter to clay mineral content changes from 0.5–0.4 to 0.4–0.2 and then to less than 0.1, the content of Mo, for instance, drops from 160–100 g/t to 75–50 g/t and 15–3 g/t, respectively. That same trend is traceable for other organophilic elements (U and Zn). In addition, the concentration of elements bound to the clastic components of the rock (Zn, Sr, Cr, and others) increases substantially from the central part to the perimeter of the basin.

In the third metallogenic type, essentially siliceous, diatomaceous formations enriched in uranium are distinguished, related to the bathyal regions of the ocean basins. In particular, the black shale-diatomites in the Miocene-Pliocene Monterey and Sisquoc Formations in southern California are of this type. According to Durham (1987), the U concentration in the shales ranges from 2.5 to 1985.0 g/t. Most of the U is in organic matter and biogenic opal; the U contained in phosphate, which forms numerous inclusions in the "nodular shales," is not more than 510 percent of the total U in the rock. The extremely low concentrations of elements other than Mo in the shales are noteworthy. The order of decreasing values of their concentration coefficients is as follows (minimum and maximum C_c): Mo (5–60), Cr (0.2–1.5), Be (0.6–1.1), U (0.2–1.0), Cu (0.3–0.8), Ni (0.1–0.7), Ga (0.3–0.5), and Co (0.1–0.4). The uranium content is not accompanied by a relatively high content of Mo or other elements. Similar uraniferous diatomite deposits have also been found on the continental slope of southwest Africa.

A geochemical phenomenon among domanikites of siliceous-carbonate composition is the Permian Phosphoria Formation (type IV) (Table 5.2), unique in concentration of P, U, and V; it occurs over a vast area of the western United States. In the lower part of the Formation, in the Mead Peak horizon, there are phosphate layers containing up to 30.5 percent P_2O_5 and 0.012 to 0.024 percent U_3O_8 (Sheldon, 1959). The accumulation of phosphorus is attributed by many investigators to an ancient upwelling zone. In Wyoming, there is a highly carbonaceous carbonate-phosphate shale member ("vanadiferous zone"), with a content of 2 percent P_2O_5, 0.56 percent V_2O_5 and 0.001–0.060 percent U. The reserves of vanadium pentoxide in this member are estimated to be 18–25 million tons (Love, 1961). Besides P and V, a broad combination of rare and disseminated elements has been found in the Phosphoria formation, among which the following predominate, on the basis of C_c: Se (660), Mo (250), Zn (87), U (37), Ni (7), and Cu (7). It is significant that redistribution of the metals throughout the formation is observed, with the formation of ore concentrations in limestone intercalations. For instance, in the Mead Peak Phosphatic deposit, individual carbonate intercalations contain up to 0.4 percent V and 0.068 percent Se.

Siliceous-carbonate domanikites with geochemical anomalies of Mo, V, Cd, Bi, Ag, and other rare and disseminated elements belong to the fifth metallogenic type (Lower to Middle Cambrian Kuonamka Formation of the Siberian platform and the Lower Cretaceous Tulebak Formation of the Australian platform). The similarity of the geologic environments in which these facies accumulated is striking: (1) area of occurrence, 700,000–750,000 km^2, with a thickness of 40–75 m; (2) occurrence of the shales in the form of isolated intercalations and members up to a few meters thick in rocks poor in organic matter; and (3) zoned distribution of deposits with different concentrations of organic matter, with a maximum content of as much as 10–34 percent in the interior of the paleobasins.

In the oil shales of the Kuonamka formation, Bakhturov, Yevtushenko, and Pereladov (1988) report that the following elements have the highest concentration coefficients (minimum and maximum C_c): Mo (19–180), Cd (13–163), Bi (30–110), V (1.5–13.0), and Ag (5–9). However, the concentrations of the elements are unevenly distributed vertically and horizontally in the basin. On the whole, the highest concentrations of V, Mo, Ag, Cd, Se, Sb, and other organophilic elements are confined to the lower shale member and to zones of the Kuonamka sedimentary basin, where the rates of deposition were minimal. Our calculations show that in these zones, the sedimentation rates during Lena and Amga time were 0.6–1.7 m/Ma, and for the lower shale member, probably even lower. According to the data of our detailed sampling, one or two ore-bearing layers of oil shale, 0.5–2.6 m thick and with average concentrations of 3000 to 5100 g/t of vanadium and 200 to 340 g/t of

molybdenum, are distinguished in the lower member, with maximum contents of 6500 g/t of V and 660 g/t of Mo. Study of the composition of the ore-bearing shales showed that they have a high content of the clay fraction (more than 77.5 vol% minus authigenic minerals), a C_{org} content of 12.5 to 34.5, and a lack of correlation between the concentrations of C_{org} and V, Se, and, in part, Mo. This last is probably governed by the fact that in early diagenesis, chemically active organic matter can bind only part of the elements sorbed from sea water, the rest being sorbed by clay minerals.

By analogy with the Olenek Basin, it can be assumed that in many basins of black shale sedimentation, the ore potential of the entire volume of oil shales is controlled by just one or two horizons, which accumulated under conditions of slower and more prolonged deposition.

In the sapropelic shales of the Tulebak formation, the concentration coefficients of organophilic elements, calculated from the data of Glikson *et al.* (1985) and Riley and Saxby (1982), have the following values: Mo (29.5–150.0), Bi (100), Cd (83), Se (50), V (6.5–25.0), Zn (7.5–10.0), U (3.5), and Ni (1.1–4.0). In individual samples, relatively high contents of Ag, Sb, and As are observed.

In the Julia Creek deposit, with oil shale reserves of 4 billion tons (220 million tons of shale resins), the content of V is 1600–2700 g/t, Ni, 140–320 g/t, and Mo, up to 270 g/t. Deep-sea drilling data are very important for interpreting the origin of black shales and determining the sources of their enrichment in metals. In recent years, much work has appeared on the composition and metal potential of oceanic black shales. As an example, we can cite data from Brumsack (1980) and Brumsack and Lew (1982) on the distribution and concentration of rare and disseminated elements in the Cretaceous black shales of the Atlantic Ocean, which correspond to siliceous-carbonate domanikites with regard to their conditions of sedimentation and composition. Calculations have shown that, first, the usual level of bio-productivity of ocean waters is sufficient for high concentrations of C_{org} to arise in black shales if sedimentation is slow, and second, the order of enrichment of black shales in Pb, Co, Cr, Ni, Cu, V, Zn, Mo, and Ag relative to clays is, except for Ag, the order of increasing concentrations of elements in normal sea water, which is the main source of heavy metals. The presence of high concentrations of Cd, Tl, and Bi in black shales also is noteworthy.

The seventh metallogenic type (Table 5.2) includes siliceous-carbonate domanikites with relatively high and anomalous primary concentrations of Re, Mo, Se, Cd, Tl, Cd, and other chalcophilic rare and disseminated elements. The so-called copper schists (Kupferschiefer) of the Central European Zechstein basin and the Lower Eocene Suzak shales of the Scythian-Turanian platform (Syr Dar'ya and Upper Amu Dar'ya Basins) are of this type. The distinguishing feature of these facies is the fact that the shales occur in them mainly in the form of single thin layers (0.25–2.20 m thick in Western Europe and 0.05–2.0 m thick in Central Asia) that persist over areas tens or hundreds of thousands of km^2. Analysis of published data (Wedepohl, 1967; Kucha, 1985; Ivanov and Poplavko, 1982) on the Kupferschiefer shows that, aside from the Cu-Zn-Pb-Ag mineralization, they contain the following set of rare and disseminated elements, listed in order of decreasing C_c values: Re (100–37,500), Se (170–500), Mo (10–460), As (13–450), Cd (15–330), Au (up to 2–50), V (2.5–35.0), and Ni (1–10). In the basal layer of the black shales, there are exceptionally high concentrations of Au and platinum-group elements (Pt, Pd, Os, and Ir). In Kucha's (1985) opinion, the concentration of gold and platinoids was the result of self-oxidation and desulfatization of organic matter. The platinum-group elements, which acted as catalysts for the oxidation process, were concentrated at a redox barrier. The radioactivity of the shales, especially that related to thucholites, intensified the process.

There are differing points of view concerning the source of the nonferrous metals in the Kupferschiefer. Wedepohl (1967) proposes a terrigenous source for the Cu, Zn, and Pb. Lur'ye (1983)

relates the formation of the mineralization to discharge of ground water from the red molasse of the "dead red [lezhnya]" into the sedimentary basin and concentration of the copper and associated metals at the shale geochemical barrier.

In the Suzak shales of the basins of Central Asia, the following elements have the highest concentration coefficients (minimum and maximum C_c): Re (880–4470), Mo (730–1450), Se (810–1000), Cd (435–790), Bi (22–100), V (15–56), Tl (20–35), Ag (11–21), and Ni (6.5–20.0) (Kler, Volkova, Gurvich *et al.*, 1987; Poplavko, Ivanov *et al.*, 1977). In the face of considerable fluctuations in the element contents for the individual areas, the order of their concentration over the whole area of occurrence of the Suzak shales remains fairly constant. In individual sections, different relationships between the organic matter content and the elements (Mo, Se,V, As, and others) are found for different concentration levels of the elements. For instance, anomalously high Mo concentrations (from 500 to 2500 g/t) fall within a relatively narrow range of variation of organic matter content (from 40 to 60 vol%), which indicates the patterns of accumulation of metals in the ore-bearing horizons established for the shales of the Olenek basin. The Suzak shales were formed in a relatively deep sea basin during the initial phase of a transgression, when rapid subsidence was not compensated by sedimentation.

Compared to domanikites, oil shale facies are acutely impoverished both in their combination of rare and disseminated elements and in the concentration of the individual elements. In clayey-carbonate oil shales (Upper Jurassic shales of the Volga and Timan-Pechora Basins, Eocene Green River Formation), mainly the rare elements Mo or Mo plus Re are found in above-clarke concentrations (Table 5.2). In some oil shale formations, locally elevated concentrations of Se, As, Au, Ag, V, and other rare elements have been found, bound in both the organic and inorganic fractions.

In the Posidonia oil shales, developed over most of the European countries (Great Britain, France, West Germany, *etc.*), the average Mo concentration is 40–80 g/t, and the concentration coefficients of other rare and disseminated elements are low: V (0.5–3.0), Ni (0.4–2.7), Co (0.6–2.0), and Cu (0.2–1.6) (Bitterli, 1960; Kunz and Bauss, 1975; Tourtelot, 1970). In the Volga oil shales, according to the data of neutron activation analysis, the order of decreasing C_c values of the elements is as follows: Mo (11–34), Se (12–15), Au (4–7), Ag (46), As (0.2–2.4), V (0.6–2.1), Ni (0.4–1.5), Sc (0.6–1.5), Sb (0.2–1.5), Co (0.5–0.6), Ce (0.5–0.6), Cr (0.3–0.5), La (0.3–0.5), and Rb (0.2–0.5). According to Kler, Volkova, Gurvich *et al.* (1987), the shales contain from 0.5 to 2 g/t Re.

In the Green River shales, with unique reserves, a low concentration of rare and disseminated elements is observed despite the high organic matter content (up to 50 percent), except for individual intercalations containing U (0.005–0.15 percent) in association with phosphates (2.2–18.2 percent P_2O_5). The presence in some oil shale deposits, for example, the Wilkins Peak Member of the Green River Formation of Colorado, of relatively high contents of Mo (30–200 g/t), as well as of Se, As, and Au is related the heavy mineral fractions of the shales, which are enriched in pyrite (Meddaugh and Salotti, 1983; Saether, Runnells, and Meglen, 1984). The impoverishment of the Green River shales in rare and disseminated elements is governed by the conditions under which they were formed, that is, in a continental (lacustrine) sedimentary environment with high rates of accumulation of the oil shales (up to 50–100 m/Ma).

To a considerable extent, also in connection with the specifics of its generation and composition, the Middle Ordovician carbonate-kukersite facies of the Baltic area has extremely low concentrations

of rare and disseminated elements. As a result of our investigations, the trace elements in the shales are in the following order of concentration: Mo (0.9), Ce (0.6), U (0.5), Sb (0.5), Sc (0.5), As (0.3), Ni (0.25), V (0.2), Co (0.2), Th (0.2), Hf (0.2), and Rb (0.1). According to published data (Kler, Volkova, Gurvich *et al.*, 1987), Re (0.05 g/t) and Mo (up to 12 g/t) have also been reported.

In clayey oil shales (late Devonian-early Permian of the Kenderlyk Basin; Eocene of the Boltysh depression; Permo-Carboniferous torbanite and tasmanite of New South Wales and Tasmania; Oligocene shales of the Fu-Shun Coal Basin; and others), the combination of rare elements and their concentration levels is governed largely by the composition of the surrounding rocks, which are the source of the clastic material. But on the whole, the content of ore elements in this type of oil shale is at the clarke level, except for some formations enriched in Mo, Be, Sc, and other rare and disseminated elements.

The above data on the distribution of rare and disseminated elements in black shales of various composition make it possible to draw the following conclusions:

1. The accumulation of rare and disseminated elements in association with organic matter and their levels of concentration are governed by the setting in which Phanerozoic black shales were formed, mainly the depositional environment and sedimentation rate. The conclusion is confirmed that the concentration of organophilic elements arose during slow absorption of an accumulation of elements from organic matter in the layer of sea water above the bottom, rather than as a result of biological activity. On the whole, the tracing of the same type of metallogenic associations at different stratigraphic levels from Cambrian to Neogene indicates that the trace-element composition of sea water was fairly constant throughout the Phanerozoic. The highest rare and disseminated element concentrations are typical of domanikite formations, which were deposited in deep-sea basins in zones that were not compensated by accumulating sediments and, correspondingly, exhibit a reduced thickness of the shale-bearing members.
2. The horizons of ore-bearing shales with economic concentrations of Mo, V, U, Ag, Re, and other rare elements were formed only in stages of extremely slow sedimentation (probably less than 1 m/Ma), with prolonged exposure of the sediments on the basin floor. Here, not only complete bonding of rare elements by chemically active organic matter occurred, but also the accumulation of the excess elements in the inorganic part of the rock, in particular, in hydromicas, phosphates and similar components, to the actual production of mineral forms. Such conditions could have been created, in particular, at the time of the initial phase of a transgression, when rapid subsidence was not compensated by sedimentation.
3. In siliceous-clayey domanikites, a close relationship is observed between organic matter and clay minerals, which even in diagenesis form single organo-montmorillonite compounds, which sorb most metals. This determines the high average concentrations of Mo (up to 135–400 g/t), U (140–340 g/t), V (up to 1500–2000 g/t), Se (up to 300 g/t), and other rare and disseminated elements and their relatively even areal distribution, with strict stratification of the mineralization throughout the stratigraphic section.
4. Because of the low content of clay material in siliceous carbonate domanikites, most of the organic matter in the domanikites remains crystallochemically unbound to the rock, which makes it possible for ore material to be redistributed and form ore concentrations in the oil shale host rocks. Moreover, the distribution of rare and disseminated elements in these siliceous-carbonate domanikites is less uniform over the area of a basin than in siliceous-clayey domanikites, and

locally high concentrations of Mo (up to 800–2600 g/t), Re (up to 5–30 g/t), V (up to 4500–6200 g/t), Se (up to 200–400 g/t), and other elements may be formed at sorption barriers, which are chiefly clayey.

5. In siliceous domanikites, with a low content of organic matter partly bound in organosilica compounds, the sorption properties of the rocks are slight, which governs the relatively low concentration of metals.
6. Domanikite facies should be considered a potential source of gold and elements of the platinum group, the concentration of which can occur at the boundary between oxidizing and reducing environments (Kucha, 1985; Shalamov, Popova, and Savitskaya, 1991).
7. In oil shale facies, the concentration of rare and disseminated elements associated with organic matter is much higher than the clarke level. This is a result of the high rates of shale accumulation, the brief period of diagenesis, and the rapid separation of the sediment from the bottom water layer. In addition, many oil shales accumulated in continental basins, and therefore lacked sea water, the main source of rare and disseminated elements.

6

POTENTIAL RARE-METAL RESOURCES IN HEAVY OIL, BITUMEN, AND OIL SHALE: A GLOBAL PREDICTION

6.1 VANADIUM AND NICKEL RESOURCES

The most common metals accompanying heavy oils and natural bitumens are vanadium and nickel, the content of which may be ten or more times greater than their clarkes and reach the level of economic ore concentrations, especially in the residual products of refining. As virtually all vanadium and nickel are concentrated in the high-boiling (>500°C) fractions during refining, the heavy residues become progressively enriched in these metals, with their maximum concentrations in the coke and ash. The vanadium concentration in the petroleum coke that results from thermal cracking may reach one percent or more, depending on the raw material, as compared to the average of 0.6 percent in iron-ore concentrate.

This circumstance, together with the development of new, highly efficient technologies for the recovery of vanadium from petroleum coke, has determined the worldwide trend in production of that metal. For instance, from 1987 to 1990 the production of vanadium from petroleum and bitumen raw material rose by a factor of 3.2, from 4,950,000 tons to 15,750,000 tons. During that same period, vanadium production from ores rose only by a factor of 1.6 (Table 6.1). Even when the raw material is imported, some countries use heavy oil rather than ore to obtain vanadium. In the United States, the importance of petroleum-derived vanadium rose from 59.4 percent in 1987 to 78.6 percent in 1990, by the use of a semifinished product obtained from the high-sulfur heavy oil of Venezuela which contains about 8 percent vanadium. In Japan, all vanadium production in 1990 was from petroleum. It should be kept in mind that during thorough refining of metalliferous heavy oil and bitumens, the coke may be enriched in Cr, Mo, Re, Au, and other metals in addition to V and Ni. For instance, our study of the coke from thermal cracking of Volga-Urals heavy oil showed that elemental concentrations as follows: V, 5500–6800 g/t, Ni, 850–970 g/t, Fe, 1900–3900 g/t, Mo, as much as 30 g/t, Cr, 30–35 g/t, Re, as much as 0.2 g/t, and Au, as much as 0.67 g/t. Obtaining polymetallic coke opens up broad prospects for the use of rare and disseminated elements in various pyrometallurgical processes.

Therefore, it is very important to determine what new metal resources are contained in heavy oil and natural bitumen, particularly V and Ni; this is especially true for countries not endowed with the traditional raw-material sources of these metals.

In appraising vanadium resources, we included in the estimate heavy oils and natural bitumens containing 180 g/t V_2O_5 (100 g/t V). This value was arbitrarily chosen at a level somewhat above the minimum economic concentration of vanadium pentoxide in crude oil (120 g/t) customarily used in estimating the reserves of V_2O_5 in a number of deposits of heavy oil in the former Soviet Union. It must be taken into account that the quality standards for vanadium in petroleum and bitumens depend on many factors, in particular the content of sulfur, asphaltene-resin components, and cokability, as well as on the extraction technology used.

Besides published analytical data on the concentrations of V and Ni in heavy oil and bitumen in various parts of the world, we also used in the appraisal our own estimates of the concentration of metals. These were based on the ascertained relationships between the elemental content and the physicochemical parameters of petroleum and bitumen in the various oil and gas basins.

The total world resources of heavy oil and natural bitumen have been estimated to be 960 billion tons (Meyer, 1987); 75 percent of the world's resources of natural bitumens are in the deposits of the Canadian asphalt belt (Athabasca, Cold Lake, Wabasca, Peace River). About two-thirds of the total world resources of heavy and extra-heavy oil are in Venezuela, with more than half of the world's resources concentrated in the Orinoco petroleum belt. As these supergiant accumulations of natural

TABLE 6.1
Trends in vanadium production, by country, for 1987 and 1990

	Vanadium production (1987)					Vanadium production (1990)				
	from ore		from petroleum			from ore		from petroleum		
Country	Amount (t)	Relative importance (%)	Amount (t)	Relative importance (%)	Total (t)	Amount (t)	Relative importance (%)	Amount (t)	Relative importance (%)	Total (t)
South Africa	27,500	100.0	–	–	27,500	35,700	100.0			35,700
USA	2700	40.6	3950	59.4	6650	3700	21.4	13,550	78.6	17,250
Japan			1000	100.0	1000			1000	100.0	1000
Canada								1200	100.0	1200
Brazil						4000	100.0			4000
Venezuela						4000	100.0			4000
Australia						2400	100.0			2400
Total	**30,200**	**85.9**	**4950**	**14.1**	**35,150**	**49,800**	**76.0**	**15,750**	**24.0**	**65,550**

bitumen and extra-heavy oil contain a relatively high concentration of vanadium, most of the vanadium contained in petroleum and bitumen in the world's balance of resources are in these deposits (Table 6.2).

According to my estimate, the world's geological reserves of vanadium in heavy oil and bitumen are about 127 million tons, which is more than twice the world's known vanadium resources in traditional ores (54.6 million tons). A number of giant deposits of natural bitumen and extra-heavy oil, which may also contain large vanadium resources, were not included in the estimate because of a lack of information on the concentration of metals in them (Meyer and Duford, 1989; Meyer and de Witt, 1990; Goldberg, 1981).

In the tar sand deposits of the Canadian asphalt belt there are at least 36 million tons of vanadium, with an average concentration of 170 g/t, and 14 million tons of nickel, with an average concentration of 66 g/t (Table 6.3). According to the Mining Journal (1985), Canada plans to obtain up to 1,000 tons of vanadium pentoxide from the ash of Athabasca bitumen, which contains 1.2 percent V_2O_5 as well as elements like Sc, Ni, Mo, and Ga.

The largest metal-bitumen province in the former Soviet Union is the Volga-Urals, where more than 85 percent of the total vanadium resource and 75 percent of the nickel resource are concentrated (Table 6.4). According to analytical data, the vanadium concentrations in the bitumen of the Ufimiam deposits range from 175 to 340 g/t and in the Kazanian deposits, 325 to 600 g/t. In the vein asphaltites of the Upper Permian complex of the Malyy Kinel' zone, the vanadium content is 2100–4830 g/t and the nickel content, 350 to 708 g/t. On the basis of the Permian bitumen resource in the Volga-Urals province, the contained vanadium resource can be estimated to be 2,216,000 tons, of which more than 694,000 tons of promising bitumen resource contains more than 5 wt%. The geologic reserves of vanadium in the proven deposits of Permian bitumens of Tatarstan are estimated to be 228,000 tons. Among the largest, with respect to vanadium pentoxide reserves, are the Akanskoye (13,700 tons), Aksubayev (19,000 tons), and Gorskoye (28,000 tons) deposits. The asphaltites of the Malyy Kinel' zone, which have anomalously high concentrations of the metals, are of greatest interest as a source of vanadium and nickel raw material.

In the Timan-Pechora province, metalliferous bitumens are confined to two zones, the Izhma-Omri and Talota-Nadeyyu. The vanadium resources in these zones are estimated to be 116,000 tons. In addition, the bitumens contain relatively high concentrations of several rare elements.

In the Lena-Anabar province, relatively high concentrations of metals have been found in the Permian bitumen of the Olenek deposit, which contains on the order of 182,000 tons of vanadium; with 140–200 g/t of V and 44–87 g/t of Ni, these concentrations are analogous to those in the bitumen of the Canadian deposits. "Undiscovered" vanadium resources may be related to the natural bitumen in a number of regions, particularly Africa (Nigeria, Zaire), the Middle East (Syria, Turkey), and possibly the United States, where the bitumen reserves are estimated to be 5.9 billion tons (Meyer, 1987).

The world's geologic resources of vanadium in extra-heavy and heavy oils are estimated to be 86.2 million tons; 19.9 million tons are recoverable as a petroleum by-product (Table 6.2). Of the total world resources of petroleum-derived vanadium, the extra-heavy oil of the Orinoco belt contains on the order of 90 percent of the recoverable resources. In planning an annual production 87 million tons of extra-heavy oils, on the order of 37,000 tons of vanadium will be recovered as a petroleum by-product every year, which can provide half the world's annual demand for that metal. The reserves are

TABLE 6.2
Estimated world resources of vanadium in heavy and extra-heavy oil and natural bitumen, by country, 1992 [Source: I.S. Goldberg]

Country	Vanadium resource (1000 t)			Limits of V concentration (average) (g/t)	Loss of V since beginning of development (1000 t)
	Natural bitumens	Heavy and extra-heavy oil			
		In-place	Recoverable		
North America					
Canada	36,700			(170)	
USA		>10	>3.2	106–360	27.60
Total	**36,700**	**>10**	**>3.2**		**27.60**
South America					
Venezuela					
Maracaibo		2196	732	116–1050	939.40
Eastern Venezuela		2082	693	129–260 (194)	
Orinoco Belt		81,175	18,275	363–489 (425)	
Ecuador		360	90	140–280	
Colombia		64	> 20	130–420	> 2.20
Peru		47	13.5	120–245 (200)	2.90
Surinam				(160)	0.05
Total		**85,924**	**> 19,823.5**		**> 944.50**
Europe-Asia					
Albania	30	10	2.5	520	
				168–285 (220)	
Italy		30	10.5	120–165 (130)	3.30
FSU	2510			140–3500	
		1543	305.3	120–1200	11.4
Total	**2540**	**1583**	**318.3**		**14.70**
Middle East					
Iraq		91	30	110–180	
Iran		50	16.5	100–150	
Syria		23	7.0	(110)	
Turkey		16	5.0	100–150	1.950
Total		**180**	**58.5**		**> 1.950**
Africa					
Egypt		53	17.5	100–135	> 20.50
Cameroon		?	?		
Nigeria	?				
Total		**> 53**	**> 17.5**		**> 20.50**
World Total	**39,240**	**> 87,750**	**> 20,0221.0**		**> 1009.00**

TABLE 6.3
Vanadium and nickel resources in the natural bitumen of the oil sands of the Western Canada Sedimentary Basin

Deposit	Age	Density of bitumen (g/cm^3)	Reserves of natural bitumen (10^6 tons)	Average content (g/t)		Resources of metals (thou. t.)	
				V	Ni	V	Ni
Western Canada Basin							
Athabasca	K_1	1.014–1.029	138,100	170	70.5	23,480	9730
Cold Lake	K_1	0.986–1.000	43,000	174	63.5	7480	2730
Wabasca	K_1	0.979–1.010	18,900	170	65.0	3213	1230
Peace River	K_1	0.935–0.010	14,600	168	65.4	2452	955
Total resources			**214,600**			**36,625**	**14,645**

expected to last 500 years. In addition, there are substantial reserves of vanadium in the heavy oil deposits of the Maracaibo and Eastern Venezuela Basins, where vanadium concentrations reach 9001150 g/t, as in the Boscan Field. In addition to Venezuela, economically valuable vanadium resources in South America are predicted in the extra-heavy oils of Ecuador ("Pungarayacu" zones) and in the heavy oils of Colombia, Peru, and Surinam (Table 6.2). On the whole, the recoverable resources of petroleum-derived vanadium in South America are about 98 percent of the world's resources, according to our estimate.

In addition, although the resources of petroleum-derived vanadium in other countries constitute a very small percentage of the huge concentrations of this metal in South America, they may be an important additional source of raw material.

In the former Soviet Union, about 64.5 percent of the recoverable resources of vanadium and 50 percent of nickel are found in the Volga-Urals province, where most of the resources are in Tatarstan and the Ul'yanovskoye region, which contain heavy oils with high average concentrations of V_2O_5 of 580 and 1028 g/t, respectively.

Among the largest in vanadium reserves are the Zimnitskoye, Novo-Yelkhovka, Aksubayevo-Moksha, Romashkino, Stepnoozerskoye, Bureyka, and other deposits and pools of heavy oil (Goldberg, Kaplan, and Ponomarev, 1986). Second in reserves of vanadium in heavy oils is the Buzachi area in Kazakhstan, where the economic reserves of this metal have already been evaluated for a group of deposits (Karazhanbas, North Buzachi, Kalamkas, and Zhalgyztyube). In the Timan-Pechora province, despite the substantial reserves of heavy oil, petroleum-derived vanadium comes to only 15 percent of the total resources of the former Soviet Union, because of the relatively low average concentrations of the metal. Estimates show that the development of heavy oil deposits with by-product recovery of vanadium and other metals in the former Soviet Union, especially in the Volga-Urals area, can substantially increase vanadium production and obtain in addition a number of valuable components, in particular vanadyl porphyrins.

TABLE 6.4
Vanadium resources in the natural bitumens in Russia

Province	Bitumen-bearing complex	Zone of bitumen accumulation	Average content of V (ppm)	Resources of V (10^3 tons)	Class of bitumen
Volga-Urals	Ufimian	West flank of S. Tatar arch	256	200	heavy oil, maltha
		Sok-Sheshma	220	130	maltha, asphalt, heavy oil
	Kazanian	Melekess	396	832	heavy oil
		Sok-Sheshma	376	187	maltha, asphalt
		Zhiguli	505	2	asphalt, asphaltite
	U. Permian	Malyy Kinel'	3350	235	asphaltite
	L. Permian	East edge of Melekess basin, west flank of S. Tatar arch	320	630	maltha, asphalt
Total for province:				**2216**	
Potential additional bitumen resources with saturation of ≥5 wt%:				**694**	
Timan-Pechora	U. Frasnian-Tournaisian	Izhma-Omri	370	33	asphalt, asphaltite
	U. Viséan-L. Permian	Talota-Nadeyyus	290	83	asphalt, asphaltite
Total for province:				**116**	
Lena-Anabar	Permian	Olenek	140	182	maltha, asphalt
Total for Russia:				**2514**	
Potential additional bitumen resources with saturation of ≥5 wt%:				**694**	

Other regions where vanadiferous petroleum with economically valuable metal resources (V and Ni) have been found are the Middle East (Iraq, Iran, Turkey, and Syria) and Africa (Egypt and possibly the Cameroon) (Table 6.2).

Considering the tendency for the amount of heavy oil and, to some extent, bitumen to increase both in the structure of reserves and in production and refining, the problem of joint development of this raw material and the possible application of useful by-product components, in particular metals (V, Ni, etc.), becomes very important.

Our estimates, based on the world's workable deposits of metalliferous and potentially metalliferous heavy oils, with calculation of the probable concentrations of V and Ni in them, have shown that since the beginning of development of these deposits, about 1,000,000 tons of vanadium and 90,000 tons of nickel have been extracted as a by-product of petroleum and virtually lost. At present world prices, that is on the order of $12.5 billion.

In Venezuela alone, about 940,000 tons of vanadium and 68,000 tons of nickel have been extracted; in the United States, 27,600 tons of vanadium and 7,200 tons of nickel; and in Egypt, more than 20,600 tons of vanadium and 11,500 tons of nickel (Table 6.2).

In addition, the lack of ecological expertise in working deposits of heavy oil containing metals (V, Ni, Zn, As, and Cd), which occur in highly toxic compounds, may lead to the danger of contaminating the environment during refining and, especially, in use of the petroleum residues.

6.2 RARE ELEMENTS IN OIL (BLACK) SHALE

According to present, very uncertain estimates, the world's resources of oil (black) shales amount to hundreds of billions to many trillions of tons. However, despite the huge oil shale resources in many parts of the world, development of the deposits is taking place slowly. Industrial and experimental work on the development of oil shale has been done in the United States, Canada, Brazil, Austria, Hungary, Estonia, Russia, China, Japan, and other countries (Knutson, Dana, Solti *et al.*, 1980). In addition to the possibility of obtaining numerous chemical products, gaseous and synthetic liquid fuels, asphalt binding materials, sulfur, and other components from oil shales, they are potential sources of rare and disseminated elements such as U, Mo, Re, V, Se, Cd, Bi, Tl, Ag, Au, Sb, Zn, Cu, and platinum-group elements (Pt, Pd, Ir, and Os).At the same time, work on the recovery of metals is also being done on a limited scale. This is largely conditioned by the technological difficulties arising because of the firm bonding of the metals to the organic matter and the inorganic part of the shales and sulfides, requiring a large consumption of chemical reagents for their recovery. It is also is related to ecological problems.

In particular, the development of the Alum shales in Sweden, which had gone on for several centuries, was discontinued in 1988 after an anti-nuclear referendum was conducted in the country and all nuclear activity was prohibited by the Swedish parliament. It is well known that the Swedish shales, rich in U, V, Mo, and other elements were used not only to obtain aluminum salts and synthetic petroleum, but also to recover rare by-product components. In the Renstad deposit, with a production of 6 million tons of shale per year, 1530 tons of U, 600 tons of Mo_2O_3, 540 tons of V_2O_5, 402,000 tons of Al, 168,000 tons of Na_2SO_4, 105,000 tons of Mg_2SO_4, and 300,000 tons of S were recovered as by-products (Anderson and Bjerle, 1988). In the Skane deposit, an attempt was made to recover vanadium from the Dictyonema shales. The technology consisted of heating the shales and gradually extracting vanadium with sulfuric acid. Because of the relatively low content of organic matter in the

rock and the low heating capacity of the shales, the petroleum was put into heating furnaces, which substantially raised the cost of the process (Andersson *et al.*, 1985).

Investigations were conducted for many years (1944–1975) on the development of methods of recovering various elements from the Dictyonema shales of Estonia (Märemäe, 1989), of which the most promising utilized sulfuric acid. Industrial use of this method was not profitable because of the very high consumption of H_2SO_4 (388 kg of 100% acid per ton of ash) and the lack of sufficiently effective ways for regenerating it. Recently, Märemäe and Taal' (1991) proposed that ammonium sulfate be used as the reagent for extracting metals from the ash of the Dictyonema shales. The extent of recovery of the metals (U, Mo, V, Tl, and Fe) from the ash in solution was 70–85 percent. However, the process for regenerating this reagent remains undeveloped.

The relatively high radioactivity of the Fammenian Chattanooga Shale in the United States, discovered in 1948, made it possible to carry out extensive investigations, including the development of technologies for separating uranium from the shale. Three ways of recovering the uranium were proposed: repeated leaching, counterflow filtering, and leaching under oxygen pressure. It was proposed that dialkylphosphoric acid be used as the reagent (Andersson *et al.*, 1985).

Coveney and Martin (1983) discussed the possibility of extracting vanadium and other metals (U, Zn, and V) from the oil shales of the Illinois basin, provided that feasible technology could be developed and deposits with higher concentrations of metals found.

In a series of test operations, vanadium with average concentrations of 2000 g/t and molybdenum with average concentrations of 270 g/t were recovered as by-products from the Australian shales of the Julia Creek deposit (Patterson *et al.*, 1986). The extraction was done by means of alkaline solutions.

At the present time, long-known silver-lead-zinc-copper deposits, those at Mansfeld, Sagerhausen, and Richelsdorf in Germany and the Lubin-Serovshan copper deposit in Poland, the largest in Europe, are targets of continuing production of metals related to the copper schists (Kupferschiefer) in the Zechstein of the Central European Basin. The nonferrous metal ores, consisting of chalcocite, bornite, chalcopyrite, galena, sphalerite, pyrite, covellite, and other sulfides, are localized in both the oil shales and, in part, in the underlying sandstones and overlying carbonate and clay-carbonate rocks (Lur'ye, 1983; Kucha, 1985). In four mines in Poland, the "Lubin," "Rudna," "Palkovice," and "Seroszovice," gold and platinum-group elements have been extracted from a centimeter-thick layer at the base of the black shales; the concentrations, especially in organic matter of the kolm type, are extremely large (as much as 3000 g/t Au, 370 g/t Pt, and 1000 g/t Pd). According to Polish geologists, annual gold production reaches 300–400 kg per year, and platinum, 10 kg.

In addition, in processing the Kupferschiefer in Germany, the dust from copper smelters is utilized, and rhenium is recovered from the formation in Finland, in the form of ammonium perrhenate.

These examples probably do not reflect all the world's experience in recovering metals from oil shales. However, it obviously can be said that at the present time the problem of developing black shales as raw material sources of rare elements mainly depends on technological, economic, and ecological factors. The development of new technologies may open up prospects for extensive commercial use of the ore components of oil shales.

At present, it is difficult to estimate the world's potential resources of rare element by-products of oil (black) shales, because of the ambiguity of estimates of shale resources and the limited and extremely uneven amount of data on the rare and disseminated element composition of the shales of

various regions. However, the estimates that have been made, even for individual regions, indicate huge reserves of rare elements (Mo, V, U, Se, Cd, Re, Tl, Ag, and others) in shales. These reserves are considerably higher than the known world resources of these elements in conventional ores (Table 6.5). The estimates include the main basins of black shale sedimentation in the former Soviet Union and Baltic area (Figure 6.1; Tables 6.6–6.8), and also, taking into account accessible information, analogous basins in the United States (Figure 6.2; Tables 6.9–6.10), Sweden, Australia, and Morocco (Tables 6.11). On the basis of this sampling, the total resources are 3,240 million tons of vanadium with a minimum average content of 0.1 percent, and 565 million tons with a minimum content of 0.2 percent; 583 million tons of molybdenum with a minimum content of $1 \cdot 10^{-2}$ percent; more than 45,000 tons of rhenium with a minimum content of $1 \cdot 10^{-5}$ percent; and 353 million tons of selenium with a minimum content of $5 \cdot 10^{-3}$ percent; (Table 6.5). The minimum contents of the elements in shales adopted for the estimate correspond to the minimum contents for which the same elements in ores are estimated quantitatively. It should be noted that many black shale facies of the world, which probably are potentially metalliferous and could be classified as deposits of the domanikite type, on the basis of composition and conditions of occurrence, were not included in the estimate for lack of information on their concentrations of rare and disseminated elements. Such facies include the Upper Permian Irati Formation of Brazil and Uruguay, which is second in the world in estimated shale reserves (1,490,000,000 tons), the Lower Carboniferous shales of Canada, the Triassic shales of Alaska, the Upper Jurassic shales of Zaire, and the Upper Cretaceous shales of Jordan, Turkey, and Israel. If we broaden the sampling, the rare and disseminated element resources in black shales can be increased many times above these estimates.

In estimating the rare and disseminated element resources in the black shales of a given basin, it must be kept in mind that economically valuable resources of V, Mo, U, Re, Tl, Cd, Ag, and other rare elements usually are related to one or two ore-bearing shale layers of no great thickness, rather than to the whole shale sequence. For instance, in the section of the Alum shales of Sweden, which has a relatively high general geochemical background of U, the economic reserves of U are related to just one shale layer 3.6–3.8 m thick, in the upper member at Renstad, which is highly enriched in the metal. In the Phosphoria basin in the United States, a so-called "vanadiferous zone" about 1 m thick, can be distinguished in the Meade Peak formation. It has an anomalous content of metals (V, Se, and U) and reserves of 18–25 million tons of vanadium pentoxide, comparable to the reserves in the Bushveld complex of South Africa (Kogan, 1979). In the Chattanooga shale in the United States, generally rich in rare and disseminated elements, the main uranium reserves are concentrated only in the upper Hathaway member, 6.0–6.9 m thick. A similar pattern is found in the Olenek Basin in Yakutia where, with a generally elevated content of V and Mo in the shales of the Kuonamka formation, a layer only 0.5–2.6 m thick in the base of the section is sharply enriched in these metals and therefore is of economic interest.

This phenomenon is manifest in basins where oil shales occur in the form of a single thin layer, as is the case with the Suzak shales of Central Asia and the Kupferschiefer of Europe. These, as a rule, are economically ore-bearing with respect to a combination of elements.

Therefore, in assessing the ore potential of the oil (black) shales of a particular basin, even in the first stage of investigation, it first is necessary to distinguish the horizon most enriched in potentially valuable components, and to trace that horizon over the area of the basin. The second task is to assess the technical economic possibilities of extracting the rare elements and to determine the minimum economic content of the rare elements as the basis for quantitative calculation of estimated resources

TABLE 6.5

Comparison of rare-element raw-material resources from conventional sources and from oil (black) shales

Element	Clarke in earth's crust[1]/ clarke in shales (%)	Lower limit of content, permitting quantitative estimation in ores (%)	Raw material resources of lithosphere[2]/ proven reserves 1987 (resources in place, 1000 tons)	World price (year end 1991) ($/t)	Lower limit of content subject to quantitative subject to estimation in solid fuels[3] (%)	Lower limit of content for which resources were estimated (%)	Potential resources in oil (black) shales (1000 tons)	Territories of occurrence of shales, on the basis of which resources of elements were estimated
Vanadium	$9 \cdot 10^{-3}$/ $1.3 \cdot 10^{-2}$	$2 \cdot 10^{-1}$	9306/54,600	11,700	$1 \cdot 10^{-2}$	$1 \cdot 10^{-1}$/ $2 \cdot 10^{-1}$	3,240,000/ 565,000	FSU[4], USA, Sweden, Estonia, Australia
Molybdenum	$1.1 \cdot 10^{-4}$/ $2 \cdot 10^{-4}$	$1 \cdot 10^{-2}$	–	4845.8	$1 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	583,000	FSU, USA, Sweden, Estonia, Australia
Rhenium	$7 \cdot 10^{-8}$	clarke in ores	3.5/9.5	140,000	$1 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	> 45	FSU, Estonia
Selenium	$5 \cdot 10^{-6}$/ $6 \cdot 10^{-5}$	$5 \cdot 10^{-4}$	102/250	11,460	$5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	353,000	USA, FSU
Cadmium	$1.3 \cdot 10^{-5}$/ $3 \cdot 10^{-6}$	$1 \cdot 10^{-3}$	585/1200	4400	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	11400	FSU, Australia
Thallium	$1 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	0.38/0.54 (1987)	44,000	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	900	Estonia, Sweden, FSU

[1] after Vinogradov (1962); [2] after Ivanov and others (1988); [3] Anonymous, 1987; [4] former Soviet Union

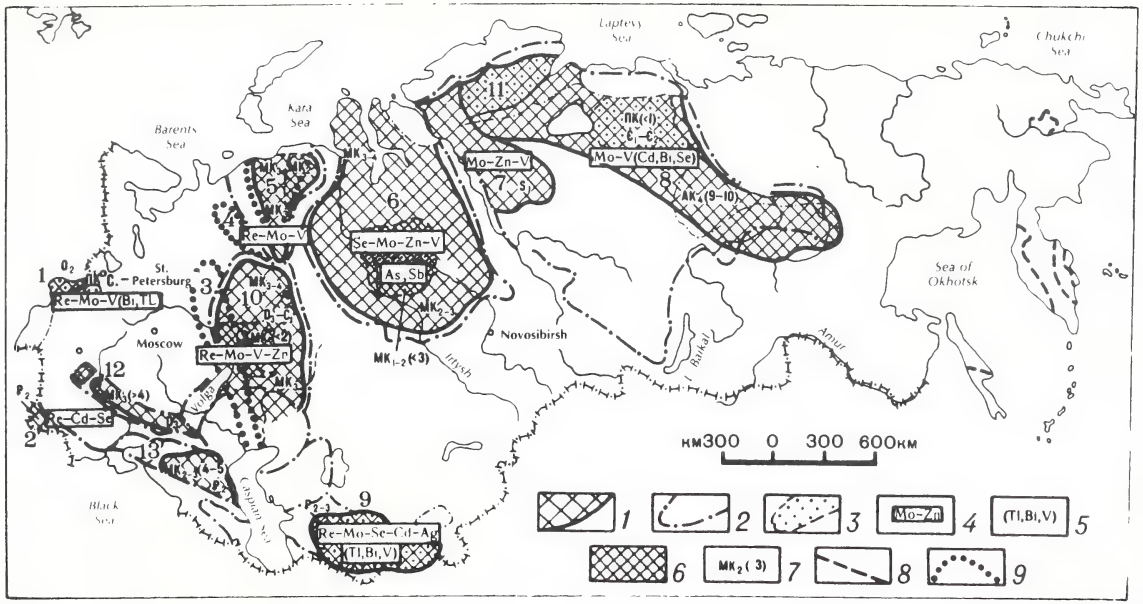


FIGURE 6.1

Metallogenic map of domanikites and oil shales in the Former Soviet Union and Baltic States [Compiler: I.S. Goldberg]

1 – Sedimentary basins with domanikites
1. Baltic
2. Carpathian
5. Timan–Pechora
6. West Siberian
7. Tungusska
8. Yudoma–Olenek
9. Syr Dar'ya and upper Amu Dar'ya
10. Volga–Ural
11. Igarka–Noril'sk
12. Dnepr–Donetsk–Pripyat
13. North Caucasus

2 – Boundaries of oil and gas basins
3 – Domanikites rich in organic matter and rare elements
4 – Main metallogenic associations
5 – Associations of elements with locally high concentrations
6 – Possible zones of generation of metalliferous petroleum
7 – Grades of catagenesis of organic matter and depth of subsidence
8 – Boundaries of oil and gas regions
9 – Boundaries of shale basins
3. Volga
4. Vyshegordk
5. Timan–Pechora

TABLE 6.6

Potential resources of rare and disseminated elements in the oil shales of the former Soviet Union and Estonia

Basin	Age, horizon, formation	Oil shale resources (million tons)	Yield of resins / OM content (%)	Resin resources (million tons)	Average concentration (g / t) / Resources (million tons)								
					Mo	Re	V	Ni	Se	Zn	Cd	Ag	Tl
Baltic, Estonia	O_1, Pakerort	62,300	3 / 5–14	1900	180 / 11.2	0.1 /	910 / 57	110 / 6.8	2.6 /	245 / 15.2	2.9 /	0.7 /	15 / 0.9
Carpathians Ukraine	P_3, Menilites	74,000	3 / 9.2	2200	33 /	0.04 /	232 17	102 / 7.5	8.0 /	99 / 7.3	2.4 /	0.3 /	–
Volga RF	J_3V_1	29,800	15 / 7–40	4500	60 /	0.15 /	230 / 6.8	150 / 4.5	9.5 /	190 / 5.6	4.5 /	0.4 /	–
Vyshegodsk RF	J_3V_1	28,000	10 / 11–15	2800	28 /	–	180 / 5	120 / 3.3	7.0 /	–	–	0.5 /	–
Timan-Pechora RF	J_3V_1	6,600	8 / 11–15	500	46 /	0.08 /	190 / 1.2	170 / 1.1	9.8 /	120 / 0.8	–	0.5 /	–
Yudoma-Olenek RF	C_1–C_2 Kuonamka	849,000	4 / 6–33	34,000	143 / 121.5	–	922 / 782	168 / 142.5	1.7 /	180 / 152	12.7 / 10.7	0.6 / 0.5	0.72 /
	C_1 lower shale number	259,000	4 / 11–33	10,360	165 / 42.7	–	2056 / 532.5	203 / 52.5	–	361 / 93.5	15.6 / 4.0	0.8 / 0.2	0.95 /
Syr Dar'ya and Upper Amu Dar'ya Tadzhikistan,	P_2 Suzak	46,900	5 / 12–31	2300	940 / 44	0.8 / 0.04	1060 / 50	218 / 10.2	59.5 / 2.8	220 / 10.3	13.5 / 0.6	0.8 / 0.04	6.0 / 0.28

TABLE 6.7
Examples of metalliferous deposits in selected basins shown in Figure 6.1

Basin no.	Field (area)	Element content (ppm)
1	Toolse	Mo-406; V-1040; Re-0.17; Ni-150
8	Dzheldinsko-Maslykay	Mo-287; V-3777; Ag-1.3; Cr-155
	Usmun	Mo-340; V-5100; Ag-1.7; Cr-160
9	Baysun	Mo-1520; V-1262; Se-78; Re-5.6[1]; TL-6.5; Ag-0.9; Ni-287; P-5250
	Urtabulak	Mo-1500[§]; Re-6.2[§]
	Bedak	Mo-1860[§]; Re-7.9[§]

[1] from Kler, and others (1987)

TABLE 6.8

Potential resources of rare elements in oil shales of selected basins shown on Figure 6.1 in the former Soviet Union and the Baltic States

Map number	Basin	Age / formation	Oil shale resources (10^6 tons)	Yield of resins / OM content (%)	Resin resources (10^6 tons)	Average concentration (g / t) / Resources (10^6 tons)								
						Mo	Re	V	Ni	Se	Zn	Cd	Ag	Tl
1	Baltic	O_1 / Pakerort	62,300	3 / 5–14	1900	180 / 11.2	0.1	910 / 57	110 / 6.8	2.6 /	245 / 15.2	2.9 /	0.7 /	15 / 0.9
2	Carpathian	P_3 / Menilite	74,000	3 / (9.2)	2200	33 /	0.04 /	232 / 17	102 / 7.5	8.0 /	99 / 7.3	2.4 /	0.3 /	–
3	Volzhian	J_3v_1	29,800	15 / 7–40	4500	60 /	0.15 /	230 / 6.8	150 / 4.5	9.5 /	190 / 5.6	4.5 /	0.4 /	–
4	Vychegodsk	J_3v_1	28,000	10 / 11–15	2800	28 /	–	180 / 5	120 / 3.3	7.0 /	–	–	0.5 /	–
5	Timan-Pechora	J_3v_1	6600	8 / 11–15	500	46 /	0.08 /	190 /	170 /	9.8 /	120 /	–	0.5 /	–
6	West Siberian	J_3v_1–K_1v / Bazhenovo	–	– / 6–15 (8)	–	122 /	–	539 /	290 /	103 /	678 /	–	1.0 /	–
7	Tungusska	S.L	–	– / (6.6)	–	24 /	–	108 /	110 /	3.5 /	–	–	0.4 /	–
8	Yodoma-Olenek	$Є_1$–$Є_2$ / Kuonamka	849,000	4 / 6–33	34,000	143 / 121.5	–	922 / 782	168 / 142.5	1.7 /	180 / 152	12.7 / 10.7	0.6 / 0.5	0.72 /
		$Є_1$ lower shale member	259,000	4 / 11–33	10,360	165 / 42.7	–	2056 / 532.5	203 / 52.5	–	361 / 93.5	15.6 / 4.0	0.8 / 0.2	0.95 /
9	Syr Dar'ya & Upper Amu Dar'ya	P_2 / Suzhak	46,900	5 / 12–31	2300	940 / 44	0.8 / 0.04	1880 / 50	218 / 10.2	59.5 / 2.8	220 / 10.3	13.5 / 0.6	0.8 / 0.04	6.0 / 0.28
Total resources, including elements			1,355,600	–	78,560	219.4+	0.04+	1450.3+	227.3+	2.8+	283.9+	15.3+	0.74+	1.18+

FIGURE 6.2

Metallogenic map of the oil shales of the United States [Compiler: I.S. Goldberg]

Age of oil shale formations

1. Tertiary
2. Tertiary Green River
3. Cretaceous
4. Triassic
5. Permian
6. Devonian and Mississippian
7. Devonian
8. Ordovician [from Dana and Roosmagi, 1988]

9 – Principal metalliferous associations

10 – Associations of elements with locally high concentrations

TABLE 6.9
Rare element content of selected metalliferous shale deposits in the United States; for locations, see Figure 6.2

Basin number	Deposit	Element content (%)
I	Temblor Range	U-0.024
II	Meade Peak phosphate	P_2O_5-30.5; U-0.012; V-0.15–0.40; Se-0.068; Mo-0.05; Zn 0.35
III	Individual layers (Σ25)	P_2O_5-2.2–18.2; U-0.005–0.15
VI_{II}	Logan Quarry	P_2O_5-1.0; U-0.024; V-0.143; Mo-0.073; Se-0.03; Zn-0.48
	Mecca Quarry	U-0.016; V-0.597; Mo-0.116; Se-0.025;

TABLE 6.10 Oil shale resources and concentrations of rare elements

Map number	Basin	State	Age, formation	Oil shale resources (10^6 tons)	Yield of resins (%)
I	Californian (Ventura, Los Angeles, etc.)	California	N_1–N_2, Monterey, Sisquoc	175,000	10–15 4–8
II	Phosphoria	Montana, Wyoming, Idaho, Utah	P, Phosphoria (Meade Peak, Retort)	500,000	7
III	Green River	Colorado, Utah, Wyoming	P_2, Green River	3,150,000	4–19
IV	Pierre Shale	South Dakota, Dakota, Nebraska	K_2, Sharon Springs	–	15
V	Appalachian		0–S		6.7
VI	Chattanooga ("Black Shale Belt"	Tennessee, Kentucky, Ohio Tennessee	D_3–C_1, Chattanooga (Hathaway, Dowelltown) Hathaway	750,000	4–10
VII	Eastern Indiana	Illinois, Indiana	C_1–C_2, Logan Quarry		
VIII	Alaskan	Alaska	T	56,000?	10–15

in oil shales in the United States; for locations, see Figure 6.2

Shale resin resources (10^6 tons)	Average concentration (g/t) / Resources (10^6 t)							Elements forming their own minerals
	Mo	V	U	Se	Ag	Ni	Zn	
140 7000	30 /	391 / 62	16 / 2.8	–	–	146 / 25	231 / 40	P, Mo
36,000	500 / 250	1500 / 750	200 / 100	400 / 200	–	700 / 350	–	P_2O_5 (2–28%); Zn, Pb
220,000 (in individual layers	200 /	–	50–150 /	–	–	–	–	P_2O_5 (2.2–18); Na, Ba, Sr, Fe, U
–	240 /	410 /	500 /	16 /	2.5 /	–	–	P_2O_5
	50 / 10?	2000 / 400?	–	–	–	–	1000 / 200?	
30,000 8000 (near surface)	200 / 150	1500 / 1125	100 / 78 4.2–5.0	200 / 150	2.0 / 1.5	200 / 150	1000 / 750	P_2O_5
	730– 1160 /	1500– 5850 /	160– 240 /	250– 300 /		450	4600	P_2O_5 (1), Zn (0.46), Pb, Cu
7000	–	–	–	–	–	–	–	

TABLE 6.11

Potential resources of rare and disseminated elements in selected foreign basins

Basin	Country	Age, formation	Resources of oil shale, (million tons)	Resin yield (%)	Resin resources (million tons)	Average concentration (g / t) / Resources (million tons)							
						Mo	V	U	Se	Ag	Ni	Zn	Cd
Baltic	Sweden	$Є_2$–O_1	71,000	5	3550	200 / 14.2	970 / 68	190 / 13.5	3.2 /	1.4 / 0.1	160 / 11.3	220 / 15.6	4.6 /
West Moroccan	Morocco	K_1 Tarfaya	14,400	6.5	2200	20 / 0.3	600 / 8.6	100 / 1.4	–	–	200 / 2.8	400 / 5.6	–
Eromanga	Australia	K_1 Toolebac	4000 (Julia Creek field)	5.5	220	270 / 1.0	2000 / 8.0	30 / 0.1	30 / 0.1	5 / 0.02	160 / 3.2	800 / 0.6	25 / 0.1

and reserves of useful by-products. Components which could lead to contamination of the environment must also be estimated quantitatively in planning utilization of the shales. This is especially important because many black shales contain metals in radioactive and highly toxic compounds. The directions in which shales can be developed for use as solid binding materials for road paving and cementing materials (Knutson, Dana, Solti *et al.*, 1988) should be accompanied by measures for demetallizing the raw material.

Systematic study of the resources of various rare and disseminated elements in black shales, on the one hand, can make it possible to increase the raw-material resources of rare elements, and, on the other, prevent the possibility of unfavorable ecological consequences in refining the shales.

7

ENHANCING THE EFFICIENCY OF JOINT DEVELOPMENT OF METALLIFEROUS HEAVY OIL AND BITUMEN DEPOSITS

To enhance the efficiency of developing deposits containing highly viscous petroleum, thermal methods of attacking the formation are widely used. In the former Soviet Union, enhanced oil recovery (EOR) by thermal methods and fire flooding are most common. Use of various modifications of these enables us to considerably increase the oil recovery of formations and to recover reserves of hydrocarbons that are difficult to extract in development. At the same time, in the face of the proven technological efficiency of thermal methods, problems of the joint development of deposits of metalliferous heavy oil and bitumen, including by-product recovery of vanadium and nickel, remain unsolved. In order to study the effect of various thermal methods of development on the extent of recovery of metals, studies were made to analyze the concentrations of vanadium and nickel in petroleum from producing wells in test-commercial firefloods and thermal EOR projects in the Karazhanbas field on the Buzachi peninsula in Kazakhstan. The targets of development were the Neocomian D and E Formations. Both formations had been drilled on the same grid of wells, and injection wells were drilled to each formation separately. According to the technological scheme, the following systems of development are used: linear one-row, linear three-row, and areal seven spot, with different densities of the well grid (100×100, 150×150 and 200×200 m). In connection with the zonal inhomogeneity of the producing formations, the test-commercial work showed that the thermal fronts and the combustion fronts migrate nonuniformly, which necessitates constant monitoring during development.

To determine the initial concentrations of vanadium and nickel in the petroleum, before thermal attack, samples from the sectors where fire-flooding had not yet been initiated were carefully analyzed. The results of the analyses showed that the average vanadium and nickel contents in Formation D are 104 and 44 g/t, respectively, and, for Formation E, 162 g/t and 50.7 g/t, respectively. These concentrations were taken as the basis for subsequent calculations.

In evaluating the effect of thermal methods on the variation in vanadium and nickel concentrations in the petroleum produced, we started from the following model. When a combustion front is formed, metals would be concentrated in the coke residue of the burning fuel. As the combustion front migrates, a zone of steam and a wall of hot water and light hydrocarbons are formed. A decrease in concentration of vanadium and nickel in the recovered product would be observed, compared to the petroleum obtained from outside the reaction zone. Then, in the zone not involved in thermal attack, the observable relative reduction in viscosity and density of the petroleum would also be reflected in a decrease in concentration of asphalt-resin components and, consequently, in the metals bound to them.

This model is fairly well confirmed by the results of investigations based on analyses of 89 samples of petroleum collected from producing wells of a fireflooded oil field. The concentrations of vanadium and nickel in the petroleum were determined, without ashing the samples, by X-ray fluorescence analysis, using a semiconducting spectrometer and X-ray tube, a procedure developed in the VNIGRI.

On the basis of the analytical data obtained, a map was compiled of the distribution of vanadium and nickel concentrations. The zones showing a loss of metals should correspond to zones with different intensities of thermal attack (Figure 7.1). The direction of the combustion fronts probably could be traced on the basis of the minimum values of concentration of metals contained in the petroleum. However, with a 200×200 m grid of wells, no sharp change in metal content could be traced from the injection to the producing wells, as the foci of combustion and zones of condensation did not reach the latter.

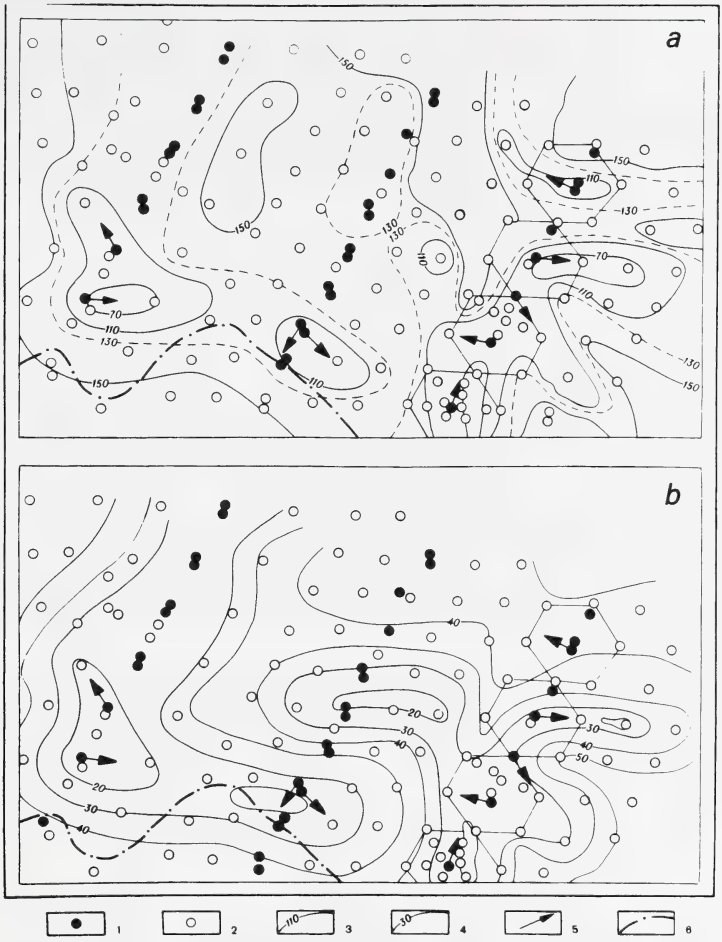


FIGURE 7.1

Distribution of vanadium (a) and nickel (b) in oil from the Karazhanbas Field, with experimental exploitation by wet combustion [Compiler: I.S. Goldberg]

1 – Injection wells
2 – Producing wells
3 – Isopleths of vanadium concentration (ppm)
4 – Isopleths of nickel concentration (ppm)
5 – Presumed path of combustion front
6 – Limit of layer G

On the whole, as a result of fire-flooding there was an irreversible loss of metals in the recovered petroleum, which amounted to an average of 36.3 percent of its recoverable reserves, but reaching 70–75 percent in zones of intensive thermal attack. After fire-flooding, the average content of vanadium and nickel in the petroleum, as a percentage of the original content, was, respectively, 39.5 and 38.6 in the zone of strong attack; 64.2 and 77.2 in the zone of medium attack; 81.5 and 91.7 in the zone of slight attack; and 100 and 100 in the zone that was not burned. The proportion of the total area to the areas of burned zones was: strong attack, 11 percent; medium attack, 61 percent; and slight attack, 28 percent. The largest zone of sharply reduced concentration of vanadium in the petroleum was related to injection wells 82, 80a, and 78, which were subjected to fire-flooding in 1981–1982. This zone also is surrounded by relatively low concentrations of nickel in the petroleum.

Calculations by Belonin, Goldberg, Gribkov, and Iskritskaya (1990) show that the damage from irreversible loss of vanadium pentoxide and nickel as a result of fire-flooding during the entire period of exploitation of the test project might have amounted to more than 40 million rubles, at the wholesale prices pertaining in 1990, when the calculations were made. Currently, it would be much greater. When fire-flooding was involved in development of the highly viscous oil on the Buzachi peninsula in the Karazhanbas, North Buzachi, and Zhalgiztyube Fields, the presumed economic damage from the loss of vanadium pentoxide was estimated to be 135.5 million rubles in 1990, including about 70 million rubles for the Karazhanbas Field.

In addition to fire-flooding, thermal EOR was applied in a test sector of the Karazhanbas field. As the studies showed, the loss of vanadium and nickel in steam heating is slight, not more than 10–15 percent of recoverable reserves. Considering that the coefficient of petroleum yield is about the same for fire-flooding and steam heat, the latter should be considered more economically justified in developing the Karazhanbas field.

Thus, the calculations presented show that developing fields with highly viscous petroleum and an economic content of metallic components, vanadium in particular, by use of fire-flooding leads to considerable economic loss, which is further aggravated by the fact that the process requires the consumption of 10–40 kg of petroleum for fuel per square meter of formation. Moreover, fire-flooding is accompanied by destructive oxidation processes, leading to a change in the chemical composition and molecular structure of the petroleum, that is, qualitatively new products are obtained which require additional stages of refining to obtain the oil components and diesel fuel.

Along with the positive effect of thermal EOR, there are negative aspects: (1) the demand for large volumes of water suitable for obtaining steam; (2) construction and operation of a steam-generating plant with a considerable energy consumption; (3) progressive flooding of recoverable petroleum at a certain stage of exploitation; and (4) difficulties in transporting the highly viscous oil that is recovered.

The methods of developing highly viscous heavy oil enriched in vanadium that are currently adopted both in the former Soviet Union and abroad do not guarantee their highly efficient joint development. Therefore, theoretical and experimental investigations were made in the search for new ways to develop vanadiferous petroleum deposits. Visbreaking, a method for thermal recovery of viscous petroleum developed by V.K. Hunt (1984; cited by Belonin, Goldberg, Gribkov, and Iskritskaya, 1990) has none of the above defects for thermal EOR, is economically more efficient, and provides more complete recovery of petroleum from the formations. The method is based on a technological combination of the processes of producing and refining viscous petroleum. It consists of

thermally refining the oil in the field and then injecting the hot light ends of the oil into the formation as a hydrocarbon-based heat carrier. With some additions and modifications, this method also will make it possible to recover useful by-product components, vanadium in particular (Belonin, Goldberg, Gribkov, and Iskritskaya, 1990). Investigations and technological-economic calculations made at the VNIGRI show that incorporation of visbreaking will make possible the more integrated development of deposits of highly viscous, economically vanadiferous petroleum and bitumen. At the same time, the question of the use of fire-flooding in such fields must be reexamined in view of the uncompensatable losses of vanadium, nickel, and other metals, the burning of part of the petroleum in the formation, and the deterioration in quality of the product recovered.

CONCLUSIONS

This book is intended to draw attention to the virtually undeveloped resources of rare and disseminated elements associated with heavy and extra-heavy petroleum, bitumen, and oil shale, which could be an important commercial source of mineral raw material. In addition, by-product recovery of metals from fossil fuels will stimulate and make profitable the development of hydrocarbon reserves that are difficult to recover.

Prediction of ore concentrations in heavy oil, bitumen, and oil shale in the former Soviet Union and other parts of the world was based on my theoretical work, which was carried out in the following directions:

1. Developing the theory of the processes of bitumen genesis and ascertaining the conditions of concentration of metals in heavy oil and bitumen of different genetic types. Studying the mode of occurrence of rare and disseminated elements in heavy oil and bitumen and their ash and the relationships of rare and disseminated element nomenclature to the geochemical types of petroleum and bitumen.
2. Classifying the bitumen regions of the world on the basis of distribution, structure, and composition of the bitumen accumulations. Ascertaining the relationship of the scale of bitumen accumulation in oil and gas basins to the tectonic evolution of the basins, the timing of bitumen formation, and the regime of tectonic evolution after the stage(s) of oil and gas accumulation (Goldberg,1981).
3. Substantiation of the metallogenic specialization of the various oil and gas provinces of the world and the possible levels of concentration of rare and disseminated elements in heavy oil and bitumen. On the basis of the dominant rare and disseminated elements in petroleum and bitumen, in terms of absolute concentration, three main types of naphthometallogenic provinces are distinguished: I, vanadium and nickel-vanadium; II, nickel and vanadium-nickel; and III, zinc. Naphthometallogenic provinces of the first type have the highest regional level of rare and disseminated element content; in these, economic concentrations of vanadium, nickel, and other metals have been found and are predicted.
4. Ascertaining the geological and geochemical conditions governing the metallogenic specialization of oil and gas basins. Two types of ore concentrations are distinguished: (1) organophilic, in which the source of the rare and disseminated elements is the ore component of organic matter of the oil-generating domanikite facies, and (2) secondarily concentrated, related to secondary enrichment of petroleum in rare and disseminated elements in vast zones of infiltration.

   For the organophilic type of naphthometallogenic province, the association and level of concentration of rare and disseminated elements is governed by the extent of catagenesis of the organic matter and the composition of the parent rocks. The boundary values of the stages of catagenesis at which certain naphthometallogenic provinces are formed have been determined: (1) PK_3–MK_2 (vanadium and nickel-vanadium); (2) MK_2–MK_3 (nickel); and (3) higher than MK_3 (zinc). The genetic relationship of the most metal-rich (V, Ni, Mo, *etc.*) heavy, "immature" oils to domanikites of low stages of catagenesis (not more than MK_1) has been brought out.

   For the secondary-concentration type of naphthometallogenic province, the rare and disseminated element association is governed by the ore content of the rocks surrounding the basin, in the catchment area of the infiltrating waters.

5. Developing genetic models of metalliferous deposits of heavy oil and bitumen. On the basis of the conditions of concentration of metals (V, Ni, Mo, *etc.*), three subtypes of organophilic deposits are distinguished: early catagenic, supergene-residual, and fractional; for each of these, certain geochemical indicators have been ascertained. Deposits of the secondarily concentrated type contain a broad combination of elements (V, Mo, Ni, U, Se, Ge, Hg, *etc.*) sorbed by high molecular weight components of heavy oil and bitumen from infiltrating waters and hydrothermal solutions, that is, concentration at physicochemical barriers.

   A difference was found in the analytical relationship between metal concentrations and the parameters of the petroleum and bitumens of the organophilic and secondarily concentrated types. In the first case, they are linear, in the second, exponential.

6. Ascertaining the dependence of the rare and disseminated element concentration on the conditions of formation and physicochemical parameters of petroleum and bitumens, which would allow calculation of the concentration of the V and Ni in deposits of heavy oil and bitumens in many of the oil and gas basins of the world.

7. Studying the patterns of distribution of metalliferous deposits of heavy oil and bitumens as well as the conditions of accumulation of the vanadium in them, for virtually all the vanadium-bearing and potentially vanadium-bearing provinces of the world, specifically the Eastern Venezuela, Maracaibo, Upper Amazon, California, Western Canada, Big Horn, Adriatic, Volga-Ural, Timan-Pechora, Persian Gulf, and Gulf of Suez Basins. Ascertaining these patterns makes it possible to predict zones where vanadiferous heavy oil and bitumen, as well as concentrations of other metals, can be found.

8. Ascertaining the geological and geochemical setting in which rare and disseminated elements accumulated in black shales, and the metallogenic specialization of domanikite and oil shale facies. It was found that rare and disseminated element associations and concentration levels are governed mainly by the environment of deposition and rate of sedimentation. Ore-bearing shale horizons with economic concentrations of Mo, V, U, Ag, Re, and other rare elements are formed only in periods of extremely slow sedimentation (probably less than 1 m/Ma) in deep-sea basins. This entails prolonged exposure of the sediments on the basin floor to the marine waters, where rare elements not only are completely bound to organic matter, but any excess elements accumulate in the mineral part of the rock. Such conditions can be created, in particular, at the time of the initial phase of a transgression, when rapid subsidence is not compensated by sedimentation.

   On the basis of rare and disseminated element associations, seven main metallogenic types are distinguished among the world's domanikite (black shale) facies: I, Mo-U-V; II, Mo-Se-Zn; III, Mo-V; IV, P-U-V (Mo, Se, Zn); V, Mo-V; VI, Ag-Mo-Zn; and VII, Re-Mo-Se. On the whole, oil shale formations proper have low concentrations of metals; this is governed by their high sedimentation rates and their frequent accumulation in freshwater and closed water bodies.

9. An estimate of the resources of elements (Mo, V, Re, U, Se, *etc.*) in the black shales of the former Soviet Union, the United States, Sweden, Estonia, Australia, and other countries has shown that they are many times higher than the known resources of these elements in traditional ores, for concentrations corresponding to industrial requirements. The inclusion of these virtually undeveloped rare-element resources for industrial use depends only on the solution to a combination of technological and ecological problems.

10. Determining the potential resources of vanadium in heavy and extra-heavy oils and bitumens, on the basis of the ascertained distribution patterns of such deposits and the known or calculated concentrations of vanadium in them. The world's geologic vanadium resources in heavy and extra-heavy oils are estimated to be 8687 million tons, on the order of 20 million tons being extractable as a by-product; in natural bitumens, there are estimated to be 39.2 million tons, which can satisfy the world demand for this metal for many years and solve the problem of providing many countries with their own vanadium resources. The main countries where deposits of economically vanadiferous petroleum and bitumens have been found or predicted to be present include Venezuela, Canada, Russia, Kazakhstan, Ecuador, Colombia, Surinam, Iraq, Iran, Syria, Turkey, Egypt, the U.S.A., Italy, and Albania. Our estimates for deposits of workable metalliferous or potentially metalliferous heavy oils in the world have shown that since these deposits began to be worked, about 1,000,000 tons of vanadium and 90,000 tons of nickel have been removed as a by-product with petroleum and virtually lost; at current world prices this amounts to something like $12.5 million.

Taken together, the postulates developed in this book provide a theoretical basis for a new specialization — the metallogeny of fossil fuels. Development of this specialization can lead to the solution of a whole combination of fundamental problems of the geology and geochemistry of caustobioliths.

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APPENDIX A

ABBREVIATIONS, ACRONYMS, AND DEFINITIONS

A (As)	–	asphaltenes
Ar	–	arenes (aromatic hydrocarbons)
IAR (MCAr)	–	monocyclic aromatic hydrocarbons
IIAR (BCAr)	–	bicyclic aromatic hydrocarbons
IIIAR (PCAr)	–	polycyclic aromatic hydrocarbons
C or K	–	carboid (resin component insoluble in chloroform)
C_c	–	concentration coefficients (clarkes)
Me	–	methane
n	–	refractive index
Nf	–	naphthene
R or T	–	resins: I, light; II, heavy
R_{AB}	–	alcohol-benzene extractable resins
R_B	–	benzene-extractable resins
R_M and R_b	–	measures of reflectance
ρ	–	density (g/cm^3)
T_M	–	melting point of bitumen
Bitumoid	–	solvent-extractable organic matter
Sulphur content	–	0.5 percent or less: low sulphur
	–	0.51–2.0 percent: sulphurous
	–	2.1 percent or more: high sulphur
IGIRGI	–	Institute of Geology and Exploration for Fuel Minerals
MNTK	–	Interdepartmental Complex for Enhanced Oil Recovery
VNIGRI	–	All-Russian Petroleum Scientific-Research Geological-Exploration Institute

APPENDIX B

STRATIGRAPHIC SYMBOLS [from Chernikov, 1988]

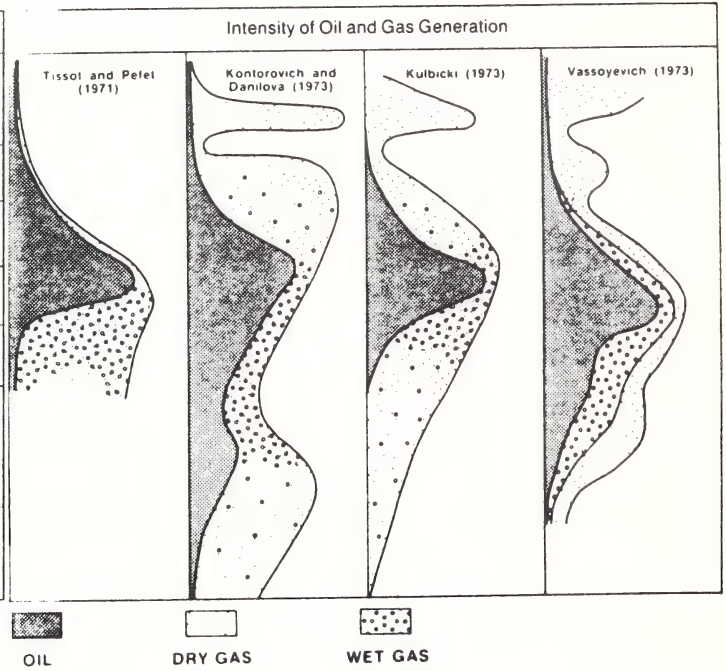
N	–	Neogene
N_2	–	Pliocene
N_1	–	Miocene
₽	–	Paleogene
₽	–	Oligocene
₽	–	Eocene
₽	–	Paleocene
K	–	Cretaceous
K_2	–	Cretaceous, Upper
K_1	–	Cretaceous, Lower
J	–	Jurassic
J_3	–	Jurassic, Upper
J_2	–	Jurassic, Middle
J_1	–	Jurassic, Lower
T	–	Triassic
T_3	–	Triassic, Upper
T_2	–	Triassic, Middle
T_1	–	Triassic, Lower
P	–	Permian
P_2	–	Permian, Upper
P_2kz_1	–	Permian, Upper, Kazanski
P_2t	–	Permian, Upper, Tatarski
P_1	–	Permian, Lower

C	–	Carboniferous
C_3	–	Carboniferous, Upper
C_2	–	Carboniferous, Middle
C_1	–	Carboniferous, Lower
C_1V	–	Carboniferous, Lower, Visean
C_1V^{bb}	–	Carboniferous, Lower, Bobrik Fm
D	–	Devonian
D_3	–	Devonian, Upper
D_2	–	Devonian, Middle
D_1	–	Devonian, Lower
S	–	Silurian
S_2	–	Silurian, Upper
S_1	–	Silurian, Lower
O	–	Ordovician
O_3	–	Ordovician, Upper
O_2	–	Ordovician, Middle
O_1	–	Ordovician, Lower
ϵ	–	Cambrian
ϵ_3	–	Cambrian, Upper
ϵ_2	–	Cambrian, Middle
ϵ_1	–	Cambrian, Lower

APPENDIX C

STAGES OF OIL AND GAS GENERATION [from Kontorovich, 1984]

Stage	Substage	Gradation	Sub-gradation	Temper-ature (°C)	Vitrinite reflect
Diagenesis		oxidizing			
		reducing			0.25
Katagenesis	proto (PK)		PK	< 50	0.53
	meso (MK)	Initial MK_1	MK^1_1	50–90	
			MK^2_1	90–135	0.65
		middle MK_2	MK_2	135–160	0.85
		deep MK_3	MK^1_3	160–185	1.20
			MK^2_3	185–200	
	apo (AK)		AK_1	200–230	2.0
			AK_2	> 230	> 3.5



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